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INTERNATIONAL SYMPOSIUM ON

Macromolecular Chemistry

Paris 1963

PART 2

Held under the auspices of the
International Union of Pure and Applied Chemistry
Paris, July 1-6, 1963

edited by *M. Magat*

Laboratoire de Chimie Physique de
la Faculte des Sciences de Paris, Paris, France

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JOURNAL OF POLYMER SCIENCE, PART C, *Polymer Symposia*

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General Lectures and Discussions which follow them and the Author and Subject Indexes will appear in Part 3 of this Symposium.

POLYMERIZATION IN THE SOLID STATE

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 767–787

Effect of Phase Transitions on Polymerization of Monomers below Their Melting Point

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Surveying a number of experimental data on the polymerization of monomers below their melting points one can distinguish two types of reactions: the first type involves "fast" reactions, which are characterized sometimes by explosion rate; the second type involves "slow" reactions in which the rate is rather small or commensurable in comparison with liquid state polymerization. The purpose of this study is to elucidate some of the reasons why fast polymerizations arise and to consider the differences between fast and slow polymerizations in solid state.

I. Fast Polymerization

More than 25 years ago Letort discovered that frozen acetaldehyde polymerized very rapidly near its melting point. It was the first example of fast polymerization in solid state described.[1–3] In 1959 we succeeded in carrying out fast polymerization of a number of monomers on the verge of the melting and even at the temperatures considerably below the melting points. This was achieved by using the method of simultaneous high vacuum condensation of monomer and inorganic compound (initiator) vapors on deeply cooled surface (molecular ray method[4]).

Active species were formed in the course of such condensation, owing to the collisions of monomer and initiator molecules either in gaseous phase or directly on the condenser surface, and trapped in the excess of frozen monomer.[5–7]

This method, in spite of some experimental difficulties, is very useful for studying solid-state polymerization and has some advantages compared with irradiation technique because (1) it is possible to vary the initiators and to choose the most specific ones for a particular monomer; (2) the temperature of the condenser surface can be varied and the solid monomer–initiator mixture can thus be obtained easily in either vitreous or in crystalline state; (3) accumulation of side products in the reaction zone (which is inevitable under irradiation) can be avoided.

The monomers and the inorganic initiators for which we could observe the fast solid-state polymerization are shown in Table I. In all cases the condenser was cooled by liquid nitrogen. At this temperature the monomer–initiator mixtures condense to form homogeneous vitreous films on the

cooled surface. The data show that the initiators act highly specifically. The metals as a rule are effective in case of monomers with electronegative substituents. On the contrary, the metal halides, which have acceptor properties, are effective for monomers with electropositive substituents. The possible mechanisms of initiation are discussed in detail in a previous paper.[6]

TABLE I

Fast Polymerization of Monomers in Frozen Molecular Mixtures[a]

	Catalysts							
Monomer	Mg	K, Na	Zn, Cd, Hg	H	NaCl, KCl	$BeCl_2$, $ZnCl_2$, $TiCl_3$	MoO_3	LiCl
α-Methylstyrene	−	−	−[b]			⊞	⊞	⊞
Isoprene	−	−	−[b]			⊞	⊞	
Styrene	−	+	−[b]	+		⊞	⊞	⊞
Acrylonitrile	⊕	⊕	+[b]	+	⊕	−	−	
Methacrylonitrile	⊕	⊕						
Methyl methacrylate	⊕			+	⊕	−	−	
Methyl acrylate	⊕					−	−	
Isopropyl acrylate	⊕							
Acrylamide	⊕							
Methacrylamide	⊕							
Vinyl acetate	+[b]							
Formaldehyde	⊕	⊕						
Acetaldehyde	⊕	⊕				−		
Acetone	⊕					−		
Butyl ester of vinylsulfonic acid	⊕					−		
Dibutyl ester vinylphosphinic acid	⊕							

[a] ⊞ = fast polymerization just at the melting point; ⊕ = fast polymerization below the melting point; + = fast polymerization, temperature unknown; − = no polymerization.

[b] The metal atoms were excited before interaction with monomer.

In connection with the subject of the present paper the most interesting were the systems in which one could observe the explosion polymerization at the temperatures considerably below the melting points of the monomers. These systems involved acrylonitrile (AN) (m.p. −83°C., explosion polymerization temperature −160°C.), methyl methacrylate (MMA) (m.p. −50°C., explosion polymerization temperature −120°C.), methacrylamide (m.p. 103°C., explosion polymerization temperature −130°C.) in combination with magnesium, etc. In all cases conversion was about 100%. For AN–Mg system it has been shown that initiation occurred in the gaseous phase owing to interaction of monomer molecules and Mg atoms resulting in formation of free radicals having a proposed structure of the type Mg—CH_2—ĊHR. The accumulation of radicals in the frozen monomer-initiator mixture was confirmed by an ESR method.[5] For following

consideration it is important that joint condensation of monomer and initiator vapors results in the formation of the vitreous monomer layer containing trapped active sites. These sites, at a suitable moment start the explosion polymerization. The problem is what is this "suitable" moment?

First of all it has been shown by special experiments that introduction of the same active species into the equilibrium monomer liquid could not

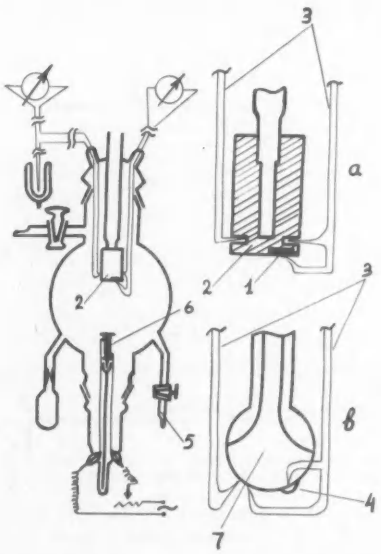

Fig. 1. Apparatus for thermal analysis of frozen molecular mixtures by (*a*) method A, (*b*) method B: (*1*) glass disk; (*2*) copper cylinder cooled with liquid nitrogen; (*3*) thermocouples; (*4*) protector of control solder of differential thermocouple; (*5*) inlet for monomer; (*6*) electrical kiln for Mg evaporation, (*7*) glass condenser.

initiate the fast polymerization.[6] Hence fast polymerization phenomena are connected with the properties of a nonequilibrium vitreous monomer–initiator mixture.

We assumed that favorable conditions for explosion polymerization are brought about by crystallization of overcooled monomer containing active species.[8,9] Such crystallization usually occurs considerably below the monomer melting point at that temperature when the time of nucleation (rate-determining step) becomes commensurable with time of experiment. In order to prove this assumption thermographic technique was used. The experiments were carried out in the device shown in Figure 1. Acrylonitrile introduced through inlet tube *5* and magnesium vapor (from electrical kiln *6*) were condensed on the surface of the glass disk attached to the bottom of the cooled copper cylinder *2* (Fig. 1*a*, method A), or on the sur-

face of a glass condenser 7 (Fig. 1*b*, method B). The use of a combination of very thin thermocouples (0.015 mm.) attached to the surface and sensitive recording potentiometers (EPP-09) permitted continuous recording of the temperature changes in the cooled monomer–initiator mixture. For taking thermographic measurements a thin (0.02–0.03 mm.) AN–Mg layer was obtained on the surface of a condenser cooled by liquid nitrogen. The rate of condensation was controlled so as to maintain a surface temperature not higher than −175°C. The AN–Mg ratio was varied in the range from 1:100 to 1:1000. In Figure 2 typical thermographic curves

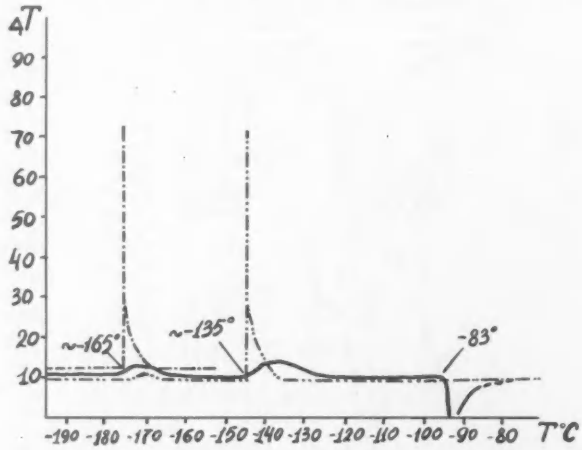

Fig. 2. Thermographic curves obtained by method A: (left to right): (*1*) and (*2*) AN + Mg; (*3*) AN; ΔT is the difference between copper cylinder and glass disk temperatures.

obtained by method A are represented. One can see that explosion exothermic polymerization occurs either at the temperature of −160°C. (curve *1*) or at a temperature of −130°C. (curve *2*), depending upon condensation conditions and rate of temperature increase. The thermographic curve of vitreous AN recorded in the same manner indicates that at these temperatures two exothermic phase transitions occur (curve *3*). The first transition (−160°C.), which is followed by dulling of the layer, corresponds to nonequilibrium crystallization of vitreous monomer film when Tamman's temperature is reached. The nature of the second transition (130°C.) is not quite clear. It is probably related to an additional ordering process in the crystalline mass. Similar thermographic curves were obtained when method B was used (Fig. 3).

As part of the study it was of interest to ascertain whether the polymerization character changed if the monomer in the initial vitreous layer was diluted with large amount of inert diluent.* For this purpose the poly-

* In this part of the study, A. N. Gvozdetsky participated.

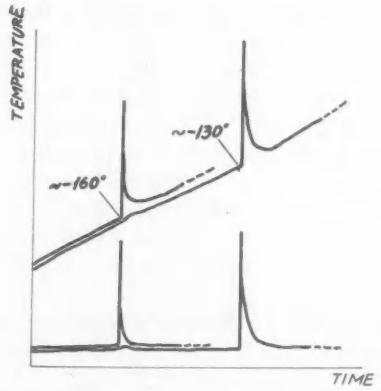

Fig. 3. Thermographic curves obtained by method B: (*1*) and (*2*) AN + Mg; (*3*) AN; (top) integral record; (bottom) differential record.

merization of acrylonitrile–*n*–hexane (AN–H) (m.p. −95.3°C.), and acrylonitrile–cyclohexane (AN–CyH) (m.p. 6.5°C.) frozen molecular mixtures in 1:10 monomer–diluent molar ratio was studied. In special study it was found that at low temperatures the systems AN–H and AN–CyH were exfoliated (Figs. 4 and 5). This means that in course of crystallization of

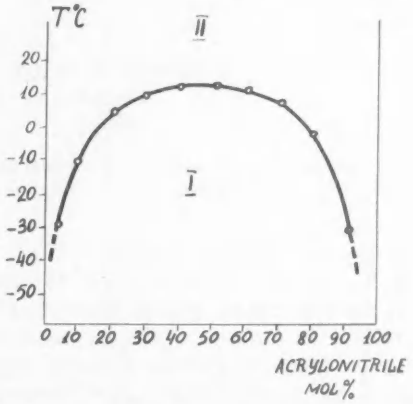

Fig. 4. Phase diagram of acrylonitrile-*n*-hexane: (*I*) solution area; (*II*) exfoliation area.

vitreous nonequilibrium mixtures two separate crystalline phases would be formed. In the series of experiments the gaseous AN–diluent mixture of strictly controlled composition and Mg vapors were simultaneously condensed on a surface cooled by liquid nitrogen. As in the case of AN without diluent, fast polymerization occurred when the nonequilibrium vitreous

layer crystallized below the melting points of both organic components. In spite of considerable dilution, AN conversion was about 100%. After melting the diluent could be quantitatively recovered and all polymer remained at the surface. Figures 6*a* and 6*b* show the polymer particles formed at the condenser surface. These particles are pseudomorphoses of AN crystals formed at the monomer–diluent mixture crystallization. It follows that fast polymerization occurs at the moment when AN separates into crystalline phase. In cases of H and CyH the picture is quite similar, although the AN melting point (−83°C.) lies between the melting points of these two diluents. The results of the experiments are shown in Table II.

If the condenser surface temperature was higher than Tamman's temperature of the monomer under study (but lower than the melting point)

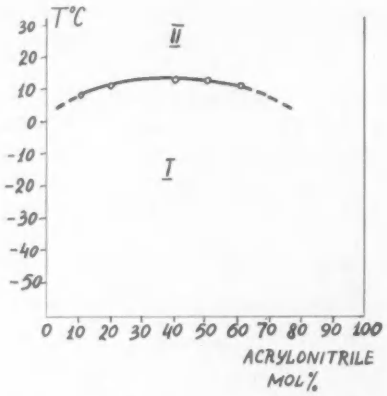

Fig. 5. Phase diagram of acrylonitrile-cyclohexane: (*I*) solution area: (*II*) exfoliation area.

the monomer molecules could migrate along the surface. Such migration was followed by nucleation and crystallization of the monomer. In this case aggregates of perfect monomer crystals characterized by typical birefringence were grown on the surface. We could observe such phenomena when the AN–Mg or MMA–Mg gaseous mixtures were condensed on surfaces cooled down to −110°C. and −75°C. respectively. The apparatus used has been described elsewhere.[4] A photograph of MMA crystalline birefringent aggregate (spherulite) formed at the condenser surface is shown in Figure 7*a*. This picture was made in polarized light by using the long-focus microscopy technique. Although the crystals contained the initiator species no fast polymerization was observed even at temperatures considerably higher than the vitreous–crystal transition temperatures of the monomers. In perfect MMA crystals at −75°C. or in AN crystals at −110°C. the very slow polymerization proceeded at a

TABLE II
Polymerization of Acrylonitrile–diluent Mixtures (Monomer–Diluent Ratio 1:10)

No.	Diluent	Duration of condensation, min.	Rate of condensation of mixture, g./min.	Mg evaporated, g.	Polymer formed		Diluent recovered		Molar ratio polymer: diluent recovered
					g.	mole × 10^3	g.	Mole × 10^3	
1	Cyclohexane	45	0.065	0.0055	0.200	3.76	3.203	38.1	1:10.2
2	"	30	0.066	0.0037	0.125	2.24	1.853	22.1	1:10.0
3	"	15	0.092	0.0053	0.082	1.55	1.302	15.5	1:10.0
4	*n*-Hexane	30	0.011	0.0055	0.168	3.17	3.007	35.0	1:11.1
5	"	30	0.007	0.0030	0.111	2.04	1.989	23.1	1:11.3

rate which was commensurable with irradiation polymerization rates of the crystalline monomers considerably below the melting points. The polymerization could be readily followed by means of the polarized light technique owing to the fact that the birefringence disappeared in the polymerized areas of the crystals. Using this technique we were able to demon-

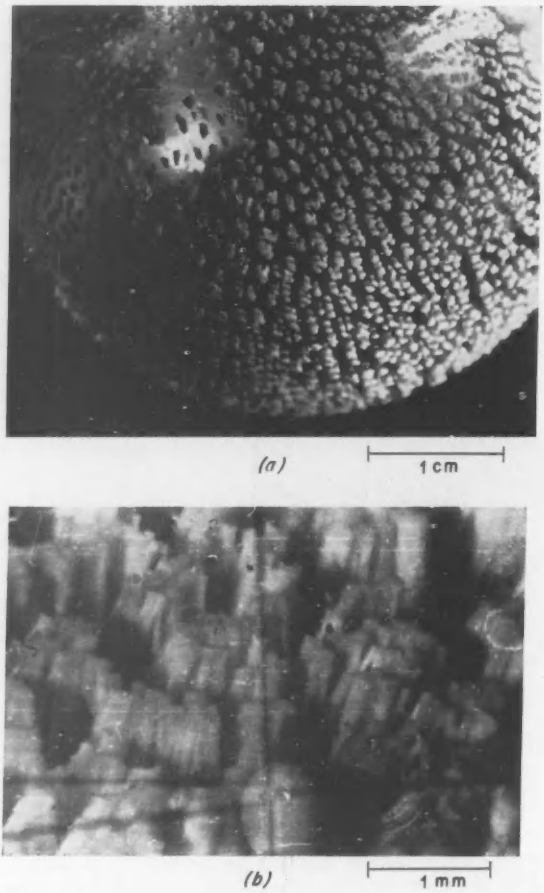

Fig. 6. Polyacrylonitrile particles on the condenser surface after melting of the diluent (*a*) hexane, (*b*) cyclohexane.

strate that the slow reaction started at the cracks or at the borders of the monomer crystals and then proceeded heterogeneously on the monomer–polymer interface. This interface could be clearly observed until polymerization was completed. The boundaries dividing polymerized and nonpolymerized areas were also clearly detected in polarized light until poly-

merization was completed (Fig. 7*b*). (This picture is very similar to that for irradiation polymerization of acrylamide described by Adler, Ballantine, and Baysal.[10]) A very sharp increase of polymerization rate was observed when the crystals were heated up to 1–2°C. below the MMA melting point. In Figure 7*c* the same spherulite as in Fig. 7*a* is shown after completion of the polymerization. (The picture was made without polaroids.)

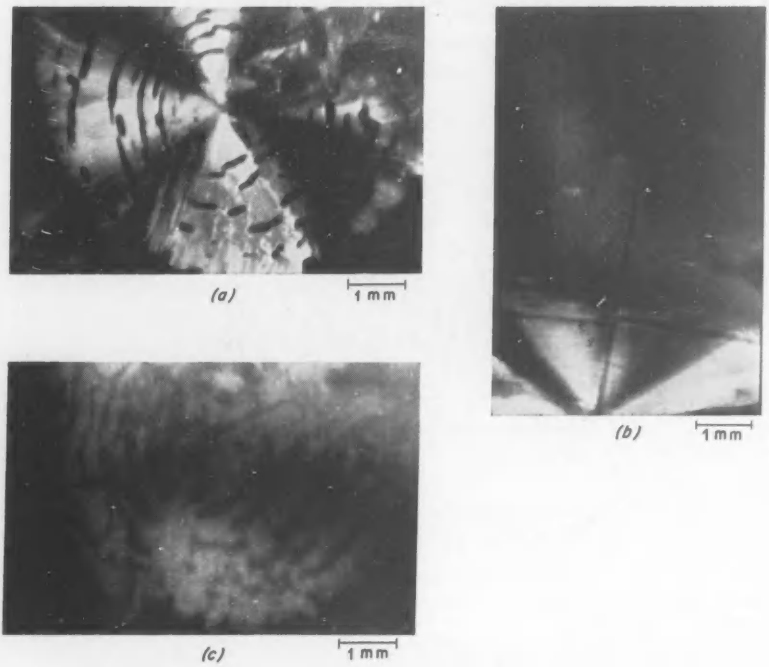

Fig. 7. Crystalline aggregates of MMA at different stages of polymerization: (*a*) before polymerization; (*b*) during polymerization; (*c*) the same area as in *a* but after polymerization was completed.

The crystalline aggregate was converted to polymer but the initial shape was not changed at all (with exception of some additional cracking owing to contraction). It is very difficult to distinguish the pseudomorphose and original spherulite without using polarized light. This fact shows that in case of good heat exchange the fast polymerization of crystalline monomers on the verge of melting is completed at the moment when the crystal has already reached the critical temperature but has not yet melted and transformed into a liquid drop.

On the basis of experimental data described, it is to be accepted that the fast polymerization in solid state is effected at a time of coordinated ordering or disordering of the monomer molecules. Apparently the ordered

arrangement of the monomer molecules combined with their coordinated mobility is the necessary condition of the instantaneous polymerization rise.[8,9] It will be noted, however, that it is not necessary to heat the entire volume of the frozen monomer up to transition temperature. In definite case, local heating is enough to effect the explosion polymerization. The local polymerization heat might be sufficient to increase the temperature within neighboring domains up to phase transition and thermal explosion arises. Such phenomena could be observed in the course of condensation of some monomers (AN, MMA, etc.) and some initiators (Mg, Na, etc.) on the surface cooled by liquid nitrogen if the condensation was carried out for a long

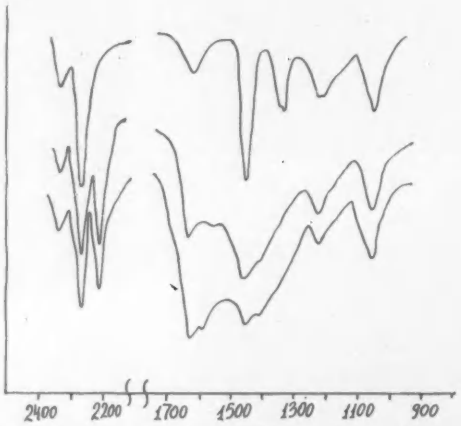

Fig. 8. Infrared spectra of polyacrylonitrile and copolymer (bottom to top): conventional radical polyacrylonitrile; polyacrylonitrile from explosion polymerization; copolymer.

time and resulted in formation of thick molecular mixture layers (owing to an increasing temperature gradient within the progressively thickened vitreous layer)[4,7,8] Apparently the formaldehyde explosion polymerization observed by Enikolopyan[11] and Magat et al.[12] was characterized by the same mechanism.

It is of interest to note that the explosion polymerization peaks on the thermographic curves did not appear at all when the temperature of monomer (AN, MMA)–initiator vitreous layer was increased very slowly. In these cases the temperature increase was followed by crystallization of the monomers, but when the "crystallization" had been completed one could find that all the monomer had converted into the polymer. This means that the nonequilibrium phase transition is the rate-determining stage of the reaction. The explosion polymerization arises as the result of the acceleration of this transition by polymerization heat formation and subsequent disturbance of the steady heat exchange.

The molecular ray method is rather convenient for study of the copolymerization of frozen monomers because it permits homogeneous vitreous mixtures, containing any two or more monomers to be obtained. Such a mixture can be used as universal original system.

The infrared spectra of polyacrylonitrile (PAN) formed as the result of fast polymerization demonstrated that the polymer contained a number of C=N bonds (1640 cm.$^{-1}$), which are practically absent in conventional radical polyacrylonitrile (Fig. 8 *a,b*). Therefore cleavage of C≡N bonds proceeded at the same time as polymerization of C—C bonds. In this connection we assumed that AN could be copolymerized with aliphatic nitriles in frozen molecular mixture. The AN–propionitrile (PN)–Mg system was used to confirm this assumption. It was demonstrated in special study that the AN–PN system is characterized with ordinary eutectic mixture of molar composition 43% AN + 57% PN (Fig. 9). There-

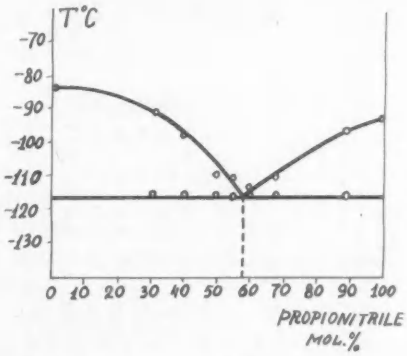

Fig. 9. Phase diagram of acrylonitrile–propionitrile system.

fore in course of crystallization of the AN–PN vitreous mixture the eutectic phase must be formed. It was also demonstrated in special experiments that no polymerization proceeded in the PN–Mg frozen molecular mixture. The data on AN–PN explosion copolymerization when the vitreous AN–PN molecular mixture containing active sites was crystallized (explosion polymerization temperature −160°C.) are summarized in Table III. (The monomer ratio was strictly controlled by using gaseous AN–PN mixture of definite composition.)

From these data one could see that PN actually copolymerizes with AN. The infrared spectrum of the copolymer also showed the presence of C=N bonds (Fig. 8*c*). The copolymer as distinct from polyacrylonitrile obtained in absence of PN is not completely soluble in dimethylformamide. The dark-red, insoluble fraction (about 50 wt.-%) was dissolved only after several hours' hydrolysis with hydrochloric acid in dimethylformamide at elevated temperature (about 70°C.).

TABLE III
Acrylonitrile (AN)-Propionitrile (PN) Copolymerization

No.	Monomer ratio AN:PN	Duration of condensation, min.	Rate of condensation of mixture, g./min.	Mg evaporated, g.	AN evaporated		Polymer formed		PN recovered		Ratio polymer recovered: PN	PN content in copolymer, mole-%
					g.	mole $\times 10^3$	g.	mole $\times 10^3$	g.	mole $\times 10^3$		
1	1:10	25	0.016	0.0032	0.034	0.65	0.051	0.96	0.34	6.17	1:6.45	32.5
2	1:10	25	0.021	0.0041	0.045	0.88	0.068	1.28	0.462	8.40	1:6.6	31
3	1:10	25	0.018	0.0036	0.040	0.75	0.063	1.19	0.390	7.10	1:5.8	37
4	1:1.35[a]	12	0.017	0.001	0.087	1.64	0.132	2.48	0.074	1.34	1:0.54	34
5	1:1.35	2	0.044	0.001	0.037	0.705	0.055	1.04	0.033	0.60	1:0.59	33
6	1:1.35	1	0.042	0.001	0.018	0.335	0.025	0.47	0.017	0.31	1:0.66	29
7	1:1.35	1	0.021	0.001	0.009	0.168	0.015	0.29	0.006	0.11	1:0.38	43

[a] Eutectic ratio.

It is remarkable that the copolymer composition within the range of experimental error was not dependent upon the initial AN–PN ratio. The evident explanation is that fast polymerization occurred within the AN–PN eutectic phase and the PN excess (when the monomer ratio is 1:10), being separated into its own crystalline phase, could not participate the polymerization.

These data confirm the conclusion that fast solid-state polymerization at phase-ordering transitions occurs at the moment when the new monomer-containing phase is already formed, but the monomer molecules have not yet lost their mobility. Discussing some aspects of the solid-state polymerization Semenov[11] assumed that in the ordered mass of monomer molecules the energetical chains could be realized. This assumption is very attractive because it explains the vigorous polymerization rate observed at very low temperatures. However, it will be noted that the most favorable conditions for "growth" of energetical chains might be realized exactly when the ordered arrangement of the monomer molecules is combined with their mobility.[9]

II. Slow Polymerization

The slow polymerization reactions in crystalline state have been the subject of extensive studies (see, e.g., references given by Magat[13]). At the present time it is generally accepted that the polymerization processes are strongly affected by the crystalline monomer lattice parameters. The main factor is the degree of correlation between monomer lattice and polymer chain parameters. If the lattice and chain parameters are essentially different, the chain growth is followed by considerable rearrangement of interatomic distances and breaking down of the lattice. Evidently in this case the propagation rate would be essentially higher if the growing chain comes in contact with already formed macromolecule or with a macromolecule aggregate which can serve as a matrix for the growing chain. In fact Adler et al.[10,14] have shown that the polymerization of some crystalline monomers mainly proceeds at the monomer–polymer interface. In such a case the polymerization process must be an autocatalytic one.

Let us consider the simplest kinetic scheme of the autocatalytical process of this type proceeding far enough from the phase transition temperature.

Initiation:

a. $$M \xrightarrow[k_i]{\sim} A$$

b. $$M + P \xrightarrow[k_i]{\sim} A' + P$$

Propagation:

a. $$A_n + M \xrightarrow[k_p]{} A_{n+1}$$

b. $$A_n^1 + M \xrightarrow[k'_p]{} A^1_{n+1}$$

Termination:

a. $$A_n + M \xrightarrow[k_t]{} P_{n+1}$$

b. $$A_n' + M \xrightarrow[k_t']{} P_{n+1}$$

where M is monomer, P is polymer chain already formed, A is active chain in the monomer molecules A is active chain in contact with polymer matrix (the same symbols will be used further to designate the concentrations of reacting particles), k_i and $k_{i'}$, k_p and $k_{p'}$, k_t and $k_{t'}$ are the rate constants of initiation, propagation, and termination characterizing the "nonmatrix" and "matrix" processes, respectively. We assume that termination occurs as a result of next monomer molecule addition providing either deactivation or "burying" of the growing chain in a rather deep trap. This correlates with the well known fact that the post-polymerization rate at temperatures far from the melting point is practically negligible in comparison with the rate of polymerization under the irradiation. Apparently termination through recombination does not play any role in such systems.

The steady-state treatment of this scheme gives the expression for polymerization rate:

$$-d[M]/dt = (\alpha + \beta[M_0])I_0[M] - \beta I_0[M]^2 \tag{1}$$

where $[M_0]$ is initial monomer concentration, I_0 is irradiation intensity, $\alpha = k_i k_p/k_t$ and $\beta = k_{i'}k_{p'}/k_{t'}$. If $\delta = \beta[M_0]/\alpha > 1$, the polymerization process is autocatalytic. The δ value shows how many times the specific rate of matrix polymerization is more than that of nonmatrix in polymerization in the monomer medium. (In some cases, if $k_i = k_{i'}[M_0]$ and $k_t - k_{t'}$, $\delta = k_{p'}/k_p$.)

Integration of eq. (1) gives:

$$Q = \frac{[M_0] - [M]}{[M_0]} = \frac{e^{\alpha I_0(1+\delta)t} - 1}{e^{\alpha I_0(1+\delta)t} + \delta} \tag{2}$$

where Q is degree of conversion. The kinetic curves described by eq. (2) for various αI_0 and δ are plotted in Figures 10 and 11. The α and β values can be estimated by treatment of experimental kinetic curves. It is easy to show that if $\delta \gg 1$, then $\ln \delta \simeq 4 \tan X\ t_m$, $\alpha = 4\tan X/\delta I_0$, and $\beta = \alpha\delta/[M_0]$, where t_m is half-conversion time and X the slope of the tangent plotted at the inflection point of the kinetic curve.

It can be shown further that weight-average degree of polymerization ($\bar{P}_w$) of the polymer formed in time interval between t and $(t + dt)$ is given by

$$\bar{P}_w = \frac{e^{\alpha I_0(1+\delta)t} + \delta}{(1+\delta)e^{\alpha I_0(1+\delta)t}} \cdot \left(\frac{k_p}{k_t}\right) + \frac{(e^{\alpha I_0(1+\delta)} - 1)\delta}{(1+\delta)e^{\alpha I_0(1+\delta)t}} \cdot \left(\frac{k_{p'}}{k_{t'}}\right) \tag{3}$$

The analysis of eq. (3) permits two important conclusions: (*1*) the molecular weight of the polymer must be increased in time if the polymeriza-

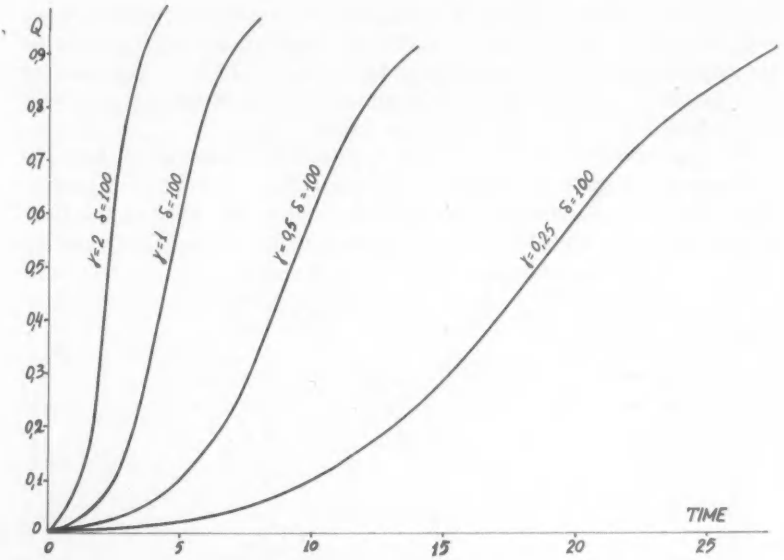

Fig. 10. Kinetic curves plotted according to eq. (2)

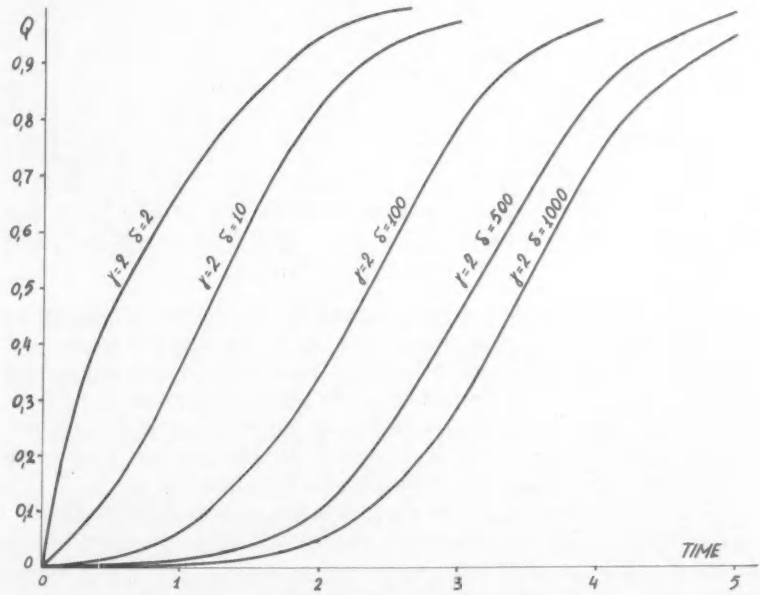

Fig. 11. Kinetic curves plotted according to eq. (2).

tion process is autocatalytic; (2) in case of the autocatalytic process, if the polymerization time is fixed, the molecular weight of the polymer must be the higher the more the irradiation intensity (I_0). The latter unusual fact may be used as an indication of the autocatalytic polymerization process if the reaction is characterized by linear termination.

The expressions written above were obtained in assumption that the polymerization reaction proceeds homogeneously. However it is easy to show that with reasonable assumptions they can be also applied to heterogeneous processes when the reaction is accelerated at the monomer–polymer

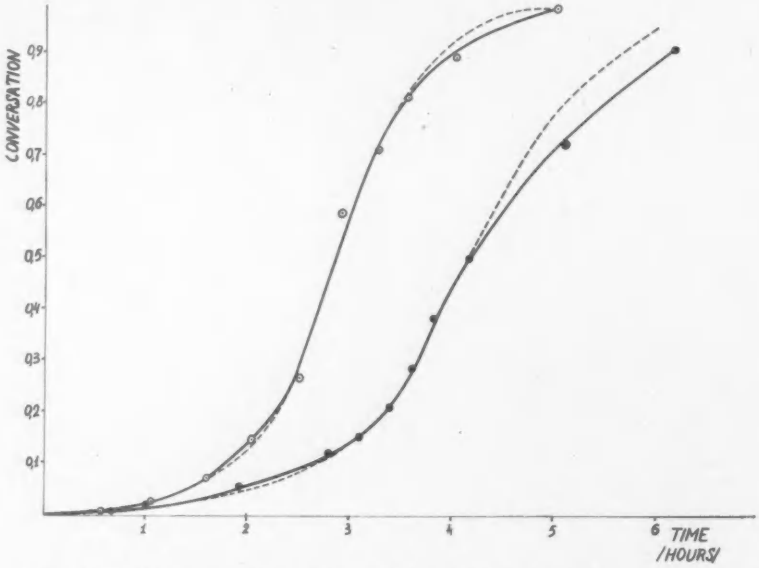

Fig. 12. Kinetics of radiation-induced polymerization of acrylamide in the solid state at 27°C. (data of Baysal et al.[14]): (⊙) I_{01} = 0.650 Mrad/hr.; (●) I_{02} = 0.410 Mrad/hr.

interface. In order to do this one must assume that the number of growing polymer nuclei in the system is proportional to the degree of conversion. Equations (1)–(3) are also valid in case of the alternative assumption that the rate of the active site formation at the polymer–monomer interface is proportional to the intensity absorbed in the entire volume of the polymer. This assumption is reasonable if in the polymer chain system there exists some mechanism of long distance excitation energy transfer.

The availability of eq. (2) for describing the solid-state polymerization at temperatures far from the phase transition temperatures could be illustrated with some unpublished experimental data, i.e., two typical kinetic curves (Fig. 12) of acrylamide irradiation polymerization obtained at the same temperature (27°C.) but at different dose rates (I_{01} = 0.650 Mrad/hr.

and $I_{02} = 0.410$ Mrad/hr.[14] From these curves $\gamma = \alpha I_0(1 + \delta)$ and δ values were estimated. For curve 1, $\gamma_1 = 2.3$, $\delta_1 = 7.6 \times 10^2$; for curve 2 $\gamma_2 = 1.55$, $\delta_2 = 6.3 \times 10^2$. The α and β constants are not dependent upon I_0. Hence at constant temperature as one could expect within the range of error that $\delta_0 = \delta_2$ and $\gamma_{01}/\gamma_2 = I_{01}/I_{02} = 1.5$. This value is in a good agreement with the experimental intensities ratio (1.6). Thus at 27°C. the rate of matrix polymerization of crystalline acrylamide (at the polymer–monomer interface) is more than 2.5 orders higher than the rate of polymerization in crystalline monomer. The kinetic curves plotted according to eq. (2) using estimated γ and δ values (dotted lines) are practically coincident with experimental ones.

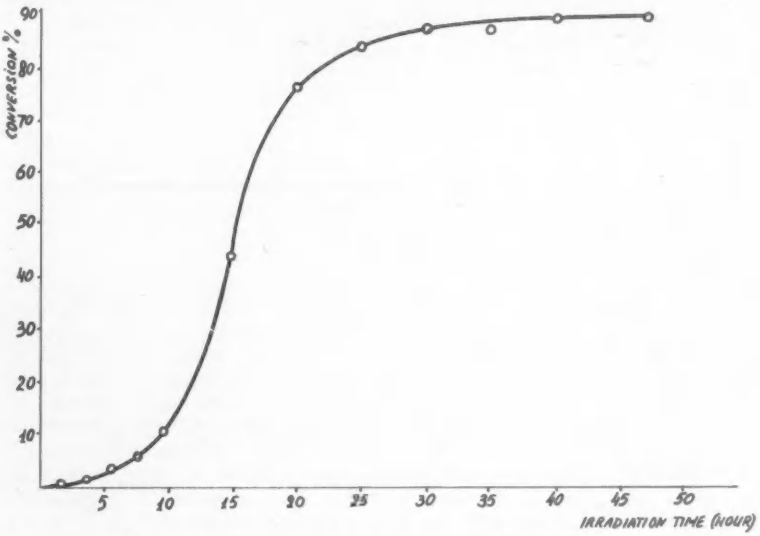

Fig. 13. Kinetics of radiation-induced polymerization of *N*-vinylsuccinimide at 20°C. $I_0 = 16800$ r/hr. (data of Hardy et al.[15]).

The kinetic of radiation-induced polymerization of crystalline *N*-vinylsuccinimide[15] is also characterized by autocatalytical acceleration. One of the kinetic curves is shown in Figure 13. The γ and δ values estimated are 0.45 and 8×10^2, respectively.

The acceleration of chain growth at the polymer–monomer interface can be explained by the mobility of higher monomer molecules in comparison with that within the crystal. This mobility is combined with the ordered arrangement of the monomer molecules at the crystal surface. In other words, at the polymer–monomer interface the kinetic conditions are similar to those at the phase transition. The possibility of aggregation of the growing chains with the already formed macromolecules provides additional advantages for the propagation reaction. The relative significance

of these interface factors is the greater, the higher are the restrictions for chain growth inside the crystal, e.g., the less favorable is the orientation of monomer molecules in the crystalline lattice. This means that the δ value (ratio of matrix and nonmatrix polymerization rates) is the higher, the more significant are hindrances for chain growth inside the monomer crystal.

If the lattice parameters are in a good correlation with the polymer chain parameters, the rates of matrix and nonmatrix polymerizations might be commensurable. Therefore δ is of order 1 and the reaction shows no auto-

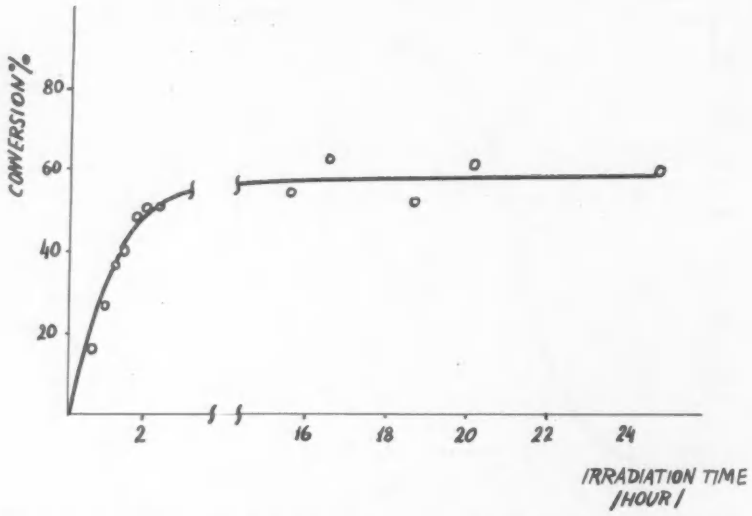

Fig. 14. Kinetics of radiation-induced polymerization of cetyl methacrylate (data of Hardy, et al.[15]).

catalytical character. Actually, in cases of monomers for which such a good correlation is proved (trioxane, β-propiolactone,[16] cetyl methacrylate,[13] etc.) the initial polymerization rates are relatively high and decrease progressively with conversion (Fig. 14).

The nonsteady explosion polymerization occurring at the phase transitions as it has been shown above (see Table I) is attributed to a number of different monomers and probably does not depend on the initial arrangement of the monomer molecules within the equilibrium crystal. This means probably that at the moment of coordinated ordering or disordering the monomer molecules necessarily pass through the favorable orientation.

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Synopsis

There exist two types of polymerization reaction of monomers below their melting point: the fast reaction (which proceeds at rates approaching the explosion rate) and the slow reaction. In the present paper these two types of reaction are studied. We succeeded in carrying out fast and slow polymerizations in the systems obtained by simultaneous condensation of monomer (acrylonitrile, methyl methacrylate) and initiator (Mg) vapors on a cooled surface. In both cases the same concentration of initiator was used. Thermographic techniques and polarization microscopy showed that the conditions of fast polymerization of the frozen monomers are essentially connected with phase state and the possibility of phase transitions on the system. The explosion polymerization of acrylonitrile (at −160°C.) and methyl methacrylate (at −100°C.) occurred during crystallization of vitreous monomers. The necessary condition for that polymerization is apparently an ordered state of monomer molecules combined with their mobility. This condition is realized at phase transitions. The polymerization of acrylonitrile in the vitreous mixtures with cyclohexane, hexane, and propionitrile was also studied. In all cases the polymerization took place during the crystallization of these mixtures. In the systems cyclohexane–acrylonitrile and hexane–acrylonitrile they crystallized as two separate phases. Regardless of the monomer/diluent ratio the polymerization proceeded up to the complete conversion of acrylonitrile into polymer. In the system acrylonitrile–propionitrile forming at the crystallization of eutectic mixture copolymerization of acrylonitrile with propionitrile occurred, the propionitrile content in the resulting copolymer being one-half of the propionitrile in the eutectic mixture. Thus it was shown that the polymerization process was closely connected with the nature of phase transitions (glass–crystal) and with the peculiarity of the phase structure at these conditions.

Résumé

Il y a deux types de réaction de polymérisation de monomères ayant lieu en dessous de leurs point de fusion: la réaction 'rapide' (approchant la vitesse d'explosion) et la réaction 'lente'. On étudie dans cet article ces deux types de réaction. Nous avons

réussi à effectuer les polymérisations rapide et lente dans des systèmes obtenus par condensation simultanée du monomère (acrylonitrile, méthacrylate de méthyle) et des vapeurs de l'initiateur (Mg) sur une surface refroidie. Dans les deux cas on a employé la même concentration en initiateur. Au moyen de la technique thermographique et de la microscopie en lumière polarisée, on montre que les conditions requises pour obtenir la polymérisation rapide des monomères gelés sont essentiellement liées à l'état de la phase at à la possibilité de transition de phase sur le système. La polymérisation explosive de l'acrylonitrile (à −160°C) et du méthacrylate de méthyle (à −100°C) a lieu pendant la cristallisation des monomères vitreux. La condition nécessaire pour obtenir une telle polymérisation est apparemment liée à l'état des molécules du monomère ainsi qu'à leur mobilité. En fait cette condition est réalisée aux transitions de phase. On a également étudié la polymérisation de l'acrylonitrile dans des mélanges vitreux avec le cyclohexane, l'hexane et le propionitrile. On a prouvé que dans tous les cas, la polymérisation a lieu pendant la cristallisation de ces mélanges. Dans les systèmes cyclohexane-acrylonitrile et hexane-acrylonitrile, il ya cristallisation en deux phases séparées. Sans tenir compte du rapport du diluant du monomère, la polymérisation a lieu lors de la conversion complète de l'acrylonitrile en polymère. Dans le système acrylonitrile-propionitrile, il se produit une copolymérisation de l'acrylonitrile avec le propionitrile lors de la cristallisation du mélange eutectique, la teneur en propionitrile dans le copolymère étant égale à la moitié de celle du propionitrile dans l'eutectique. On montre par conséquent que le processus de polymérisation est intimement lié à la nature des transitions de phase (vitreux-cristal) et aux particularités structurales des phases qui ont été formées dans ces conditions.

Zusammenfassung

Für die Polymerisation von Monomeren unterhalb ihres Schmelzpunktes gibt es zwei Reaktionstypen: die "schnelle" Reaktion (nähert sich der Explosionsgeschwindigkeit) und die "langsame" Reaktion. In der vorliegenden Arbeit wurden diese beiden Reaktionstypen untersucht. Es gelang, schnelle und langsame Polymerisationen in den durch gleichzeitige Kondensation von Monomer-(Acrylnitrile, Methylmethacrylat)- und Starter-(Mg)-Dämpfen an gekühlten Oberflächen erhaltenen Systemen durchzuführen. In beiden Fällen wurde die gleiche Starterkonzentration verwendent. Mit einem thermographischen Verfahren und mit dem Polarisationsmikroskop wurde gezeigt, dass die Bedingungen für die schnelle Polymerisation gefrorener Monomerer wesentlich mit dem Phasenzustand und der Möglichkeit von Phasenumwandlungen im System zusammenhängen. Die explosive Polymerisation von Acrylnitril (bei −160°C) und methylmethacrylat (bei −100°C) trat während der Kristallisation des glasartigen Monomeren auf. Die notwendige Voraussetzung für diese Polymerisation ist offenbar ein geordneter Zustand der Monomermoleküle verbunden mit deren Beweglichkeit. Diese Voraussetzung ist in der Tat bei Phasenumwandlungen erfüllt. Weiters wurde die Polymerisation von Acrylnitrile in glasartiger Mischung mit Cyclohexan, Hexan und Propionitril untersucht. Es wurde festgestellt, dass in allen Fällen die Polymerisation während der Kristallisation dieser Mischungen eintritt. Bei allen Monomer-Verdünnungsmittel-Verhältnissen schritt die Polymerisation bis zur völligen Umwandlung des Acrylnitrils ins Polymere fort. In dem Acrylnitril-Propionitril-System, das sich bei der Kristallisation einer eutektischen Mischung bildete, trat Copolymerisation von Acrylnitril und Propionitril auf, wobei der Propionitrilgehalt des entstehenden Copolymeren halb so gross wie der im Eutektikum war. So wurde gezeigt, dass der Polymerisationsprozess mit der Natur der Phasenumwandlung (Glas-Kristall) und mit den Besonderheiten der Struktur der sich unter diesen Bedingungen bildenden Phasen eng verknüpft ist.

Discussion

H. Morawetz (*Polytechnic Institute, Brooklyn, N. Y.*): I cannot agree with the kinetic scheme advanced in this communication for "slow" solid state polymerization. We have shown (Fadner and Morawetz, *J. Polymer Sci.*, **45**, 475 (1960)) that in the post-

polymerization of acrylamide, the molecular weight of the polymer depends only on the polymerization time, but *not* on the radiation dose, so that chains grow at the same rate no matter how many of them are growing, i.e., at widely different polymer content. The rate of in-source-polymerization may be predicted fairly well from post-polymerization rate, so that the mechanism is the same in both cases. It seems quite futile to try to interpret these kinetics by a simple scheme, since we know that the reaction rate is highly dependent on strains in crystals and reproducibility is achieved only by statistical averaging in polycrystalline samples. At any rate, any attempt at a kinetic theory should be supported by molecular weight data and runs carried out over a wide range of conditions. The statement that post-polymerization effects are negligible for in-source-polymerization is quite inconsistent with our data. Finally, it should be noted that in the data by Baysal et al. used by the authors for comparison with their theory, the polymerization rate attains values as high as 1%/min. No reliable thermostaticity is conceivable for such rates even in liquid phase polymerization, not to speak of a process where heat has to be dissipated by conduction through a solid.

V. A. Kabanov: In our kinetic scheme of 'slow" solid-state polymerization we take into account the experimental fact that in some cases the polymerization is accelerated on the monomer–polymer interface. Such interface acceleration is typical for many other solid state reactions. This is why I think that our scheme is a better approximation than those proposed before. No doubt that the question of applicability of the scheme advanced can be finally solved only when more experimental data will be available. Nevertheless I do not think that Prof. Morawetz's objections are forceable because:

(*1*) Our theory is developed for in-source-polymerization. So the molecular weight data obtained in post-polymerization study could be used as argument neither for nor against the theory. The solid-state post-polymerization in assumption of interface acceleration is the special rather complicated subject for kinetic treatment. So I cannot predict the theoretical relationship between molecular weight and preirradiation dose in that case.

(*2*) It is true that in-source-polymerization rate depends on the stresses in monomer crystals. However the reason of that dependence is connected probably with different conditions for polymerization on monomer–polymer interface, which are actually included into parameter δ. As for the dependence of polymerization rate on crystal size and reproducibility of kinetic data I do not know if in all cases such dependence are very strong. For example, Fadner and Morawetz (*J. Polymer Sci.*, **45**, 475 1960) found that the rates of polymerization of acrylamide powder and large acrylamide crystals obtained by slow cooling of acrylamide, are very close. It does not mean of course that I deny the effect of strains in monomer crystals but I think such effect could be avoided by preparing the samples in standard conditions.

(*3*) When we assume that post-polymerization rate is negligible in comparison with insource-polymerization, we mean in particular the data by Baysal et al. (*J. Polymer Sci.*, **44**, 117, 1960) and by Fadner and Morawetz (*J. Polymer Sci.*, **45**, 475, 1960). These authors found that the post-polymerization rate which could be measured is about 10^{-3}%/min. The in-source-polymerization rate at the same temperature is 10–1000 times higher. This effect is probably connected with rather fast trapping of propagating species into relatively deep traps. The probability of release of the trapped active species at a given temperature is small and increases only when the temperature is raised. So when the γ-source is removed the polymerization rate at the same temperature decreases rapidly up to relatively small value. These considerations can be accepted as steady state treatment substantiation.

(*4*) Baysal et al. described their polymerization as isothermal one. I don't know if they measured the temperature inside the polycrystalline monomer powder, but I can mention also the kinetic data by Hardy et al. presented on this Symposium. These data undoubtedly indicate that the acceleration in course of solid-state polymerization takes place in practically isothermal conditions and cannot be explained only by temperature rising.

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Polymerization in the Crystalline State. IV. Calcium Acrylate and Barium Methacrylate*

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I. INTRODUCTION

Among the criteria which may be used to infer the role played by the geometrical disposition of reagent molecules in a crystal lattice in solid state reactions, two are of particular importance. The first concerns the relative reactivities of reagents which are chemically similar and would react at similar rates if the reaction were taking place in a disordered phase. If it is then observed that solid-state reactions of such similar reagents have very different reactivities, it is reasonable to assign the difference to a more or less favorable steric disposition of the reactive groups in the various crystal structures. A special case concerns the solid-state reactivity of allotropic crystalline forms of the same reagent. It has long been known that different modifications of solid inorganic reagents may differ greatly in reactivity,[1] and a similar phenomenon has more recently been observed with an organic reagent, when it was found that two crystal modifications of choline chloride differ by a very large factor in their sensitivity to ionizing radiation.[2,3] The second criterion of the role of the crystal lattice in solid state reactions concerns the nature of the reaction product. Several cases are known where a reaction carried out in the crystalline state leads to a different product than the same reaction taking place in the liquid state. Sluyterman and his collaborators found that tetraglycine methyl ester heated in solution yields polyglycine, while heating of the crystalline reagent leads to sarcosyltriglycine.[4,5] Similarly, Prelog et al. found that the decomposition of cyclodecyl tosylate in solution led predominantly to *trans*-cyclodecene, while decomposition of the crystalline reagent yielded exclusively the *cis* isomer.[6]

In the field of solid-state polymerization both of the criteria outlined above have been applied. It was observed that potassium acrylate polymerizes, after exposure to ionizing radiation, many orders of magnitude more rapidly than the sodium or lithium acrylate and since the reaction involves only the acrylate ion, it was concluded that the difference in the

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reactivity of the salts must be due to differences in their crystal structure.[7] As for the nature of the reaction product, it was found that the solid-state polymerization of methacrylic acid leads to a chain with a tacticity strikingly different from that found in poly(methacrylic acid) obtained in solution.[8]

In the present study the scope of both approaches has been greatly extended. Calcium acrylate proved to be a very suitable subject for investigation, since it could be obtained in a number of different crystalline or amorphous modifications. These materials were used to study the relative polymerizabilities after low temperature irradiations with gamma rays. For one of the modifications, calcium acrylate dihydrate, the crystal structure was determined from x-ray diffraction data. Another monomer salt, barium methacrylate dihydrate, was used to study the tacticity of the polymer produced in various stages of the reaction.

II. RESULTS

Modifications of Calcium Acrylate and Barium Methacrylate

Calcium acrylate could be prepared in a number of crystalline modifications, anhydrous or hydrated. In addition, amorphous anhydrous calcium acrylate could be obtained by rapid dehydration of two hydrated forms. Two forms of barium methacrylate, the dihydrate and the crystalline anhydrous salt were also subjects of study. A detailed description of the preparation of these materials is given in the experimental section.

Polymerizability

The kinetic pattern of the post-polymerization of calcium acrylate samples irradiated with γ-rays at low temperature was similar to that observed previously with acrylamide[9] and alkali metal acrylates.[7] The rates were highest at the outset of the reaction and decayed rapidly thereafter. The yields for long polymerization times were linear in the logarithm of time. On the other hand, with irradiated barium methacrylate dihydrate, post-polymerization at 50°C. was characterized by an induction period similar to that observed previously with sodium methacrylate.[7] At temperatures of 101 and 120°C. the polymerization rapidly attains a limiting conversion because of the concurrent dehydration of the hydrate to the unreactive anhydrous salt.

Of particular interest in the present study was the variation of the monomer conversion obtained from the various modifications of calcium acrylate after long polymerization times. It should be noted that for all the calcium acrylates prepared the polymerization rate is very small after a period of about 150 hr. Table I lists the highest observed conversions for the calcium acrylates along with crystallographic data indicating that these salts, in fact, have different crystal structures.

Three very interesting observations can be made from the data on the different forms of calcium acrylate listed in Table I:

TABLE I

Polymerizability of Various Calcium and Barium Salts and their X-Ray Powder Patterns (2θ Values Between 6° and 15° only)

Compound	Intensity of x-ray reflections	2θ (θ equal to Bragg angle)	Polymer yield %[a] 50°C.	101°C.
Calcium acrylate dihydrate[c]	Heavy	8.55	25	52[b]
	Medium	12.49		
	Light	14.09		
Calcium acrylate monohydrate	Heavy	9.20	~0	~0[d]
	Heavy	11.36		
	Light	12.73		
Anhydrous calcium acrylate (prepared from monohydrate)	Medium	6.38	~0	14
	Light	7.20		
	Heavy	8.53		
	Medium	9.75		
	Medium	11.03		
	Medium	12.00		
	Light	14.84		
Anhydrous calcium acrylate (prepared from dihydrate)	Medium	6.74		53
	Heavy	8.47		
	Heavy	10.00		
	Light	12.53		
	Medium	14.78		
"Amorphous" anhydrous calcium acrylate (Prepared from monohydrate)	Heavy (diffuse)	8.4	12	23
(Prepared from dihydrate)	Heavy (diffuse)	8.4	50	90
Barium methacrylate dihydrate[e]	Heavy	7.80	55	44[b]
	Light	13.80		
Anhydrous barium methacrylate	Heavy	7.50	1	1
	Heavy	14.98		

[a] For polymerization times between 150 and 500 hr. (highest observed conversion). Dose 0.8 Mrad.

[b] Monomer hydrate rapidly decomposes at these temperatures.

[c] X-ray reflections of calcium salts were taken with Debye-Scherrer film cameras.

[d] No yield for 88 hr. at 101°C., then decomposition of hydrate causes polymerization to 13%.

[e] X-ray reflections of barium salts were taken with an automatic recording diffractometer.

(*1*) the degree of hydration is not the factor determining the extent of polymerization, since both the crystalline anhydrous forms and the dihydrate polymerize more extensively than the monohydrate; (*2*) the two crystalline anhydrous forms have a strikingly different polymerizability; (*3*) the "amorphous" salt made from the monohydrate polymerizes far less than the "amorphous" salt made from the dihydrate. This difference suggests that the amorphous salt retains some elements of the short range order of the structure from which it was derived.

The data in Table I also demonstrate that the dihydrate of barium methacrylate polymerizes to a far greater extent than the anhydrous salt.

Crystal Structure of Calcium Acrylate Dihydrate and Barium Methacrylate Dihydrate

It has been stated repeatedly that the determination of the complete crystal structure of a polymerizable vinyl monomer is essential to the understanding of the geometric requirements of polymerization reactions in the crystalline state. We are now in a position to propose a structure for calcium acrylate dihydrate[10] and to make an educated guess as to the crystal structure of barium methacrylate dihydrate.

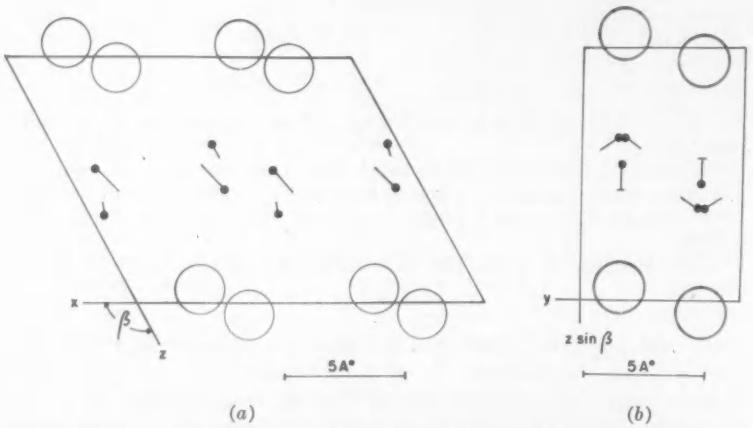
Calcium acrylate dihydrate is monoclinic, space group $P2_1/a$, $a = 14.36$ A., $b = 6.59$ A., $c = 11.62$ A., $\beta = 118.9°$. There are four molecules per unit cell, and the x-ray density is 1.506 g./cc.

The electron density distributions (ρ) projected along the b and a axes were determined from the corrected experimental relative intensities (I) of x-ray reflections from a single crystal, by performing the summations:

$$\rho_{x,z} = \sum_h \sum_l F_{h0l} \cos 2\pi (hx + lz) \tag{1}$$

$$\rho_{y,z \sin \beta} = \sum_h \sum_l F_{0kl} \cos 2\pi (ky + lz) \tag{2}$$

Here x, y, and z are fractions of the unit cell in the a, b, and c directions, respectively; h, k, and l are the Miller indices; and F_{hkl} is proportional to $I_{hkl}^{1/2}$.



(a) (b)

Fig. 1. Schematic representation of the calcium acrylate dihydrate unit cell: (a) projection onto the x,z plane; (b) projection onto the $y,z \sin \beta$ plane. Heavy lines represent vinyl groups with the substituted ends represented by solid circles. Large open circles represent calcium ions. Crossed heavy lines represent two superimposed vinyl groups; concentric open circles superimposed calcium ions.

The results of these summations are schematically represented in Figures 1*a* and 1*b*. For simplicity only the calcium ions and the projections of the vinyl groups are shown, with the substituted ends of the vinyl groups indicated by the solid circles.

The most interesting feature of the crystal structure of calcium acrylate dihydrate demonstrated in Figures 1*a* and 1*b* is the layer structure of the crystal. The calcium ions and the vinyl groups lie in sections of approximately 3 A. thickness perpendicular to the $c \sin \beta$ direction. The sections containing the calcium ions are centered around $z = 0$ and those containing the vinyl groups around $z = {}^1/_2$. It should be noted particularly that the acrylate double bonds in one section are separated by a distance of at least 7 A. from those in the next section.

The electron density projection onto the *ac* plane, was also determined by use of *h*0*l* x-ray intensity data taken with the original single crystal of calcium acrylate dihydrate after polymerization to approximately 10% conversion. This electron density map gives the same atomic positions as the corresponding map for the original crystal, the only difference being a reduction of peak height of the electron density by about 40%.

The second salt studied in detail by x-ray crystallography was barium methacrylate dihydrate which is also monoclinic, space groups $P2_1/a$, $a = 7.75$ A., $b = 12.1$ A., $c = 11.5$ A., $\beta = 90°30'$. Like calcium acrylate dihydrate there are four molecules per unit cell. The x-ray density is 2.12 g./cc. Since β is very close to 90°, the unit cell is pseudo orthorhombic, space group P_{bam}.

Projections of the electron density along the *c* and *a* axes have been obtained from the intensities of x-ray reflections from a single crystal in the *hk*0 and 0*kl* planes of reciprocal space respectively. Since most of the scattering is attributable to the barium atoms, it is very difficult to determine the exact positions of the methacrylate groups. However, the barium positions have been determined in three dimensions and this information, in addition to the eight secondary electron density peaks found in the projection along the *c* axis, allows one to make an informed guess as to the methacrylate positions. Table II lists the coordinates for the barium ions.

One can see from Table II that the centers of the barium ions lie close to $z = 0$. These planes of barium ions are separated by a distance of 11.5 A. It is reasonable to assume that the methacrylate groups will be packed in the space between barium planes so that the carboxylate groups will be

TABLE II
Positions of Barium Ions in Barium Methacrylate Dihydrate

	x	*y*	*z*
1	0.14	0.16	0.01
2	0.86	0.84	0.99
3	0.36	0.66	0.99
4	0.64	0.34	0.01

closest to the barium atoms, with the longest dimension of the methacrylate ion lying parallel to the c-direction. This would place the methacrylate double bonds in a narrow section perpendicular to the c axis centered at $z = 1/2$. This is in agreement with the eight secondary electron density peaks found in the projection along the c axis, which could then be interpreted as the projection of the length of the methacrylate ion extended in the c-direction, onto the $a \sin \beta$, b plane.

The general arrangement of the barium methacrylate dihydrate unit cell is very similar to the known structure of calcium acrylate dihydrate. The two crystals belong to the same space group and have the same number of molecules in the unit cell. Symmetry considerations would then dictate that the relation of the methacrylate double bonds to one another in the barium salt be the same as that of the acrylate double bonds in the calcium salt, although distances might be slightly different.

The intensities of the diffraction spots of barium methacrylate dihydrate were found to retain a constant ratio during polymerization at 50°C. In these experiments the monomer conversion was carried to 25 and 50%. It may then be concluded that here, just as with calcium acrylate dihydrate, no systematic changes in atomic positions occur in the crystalline residue of the monomer.

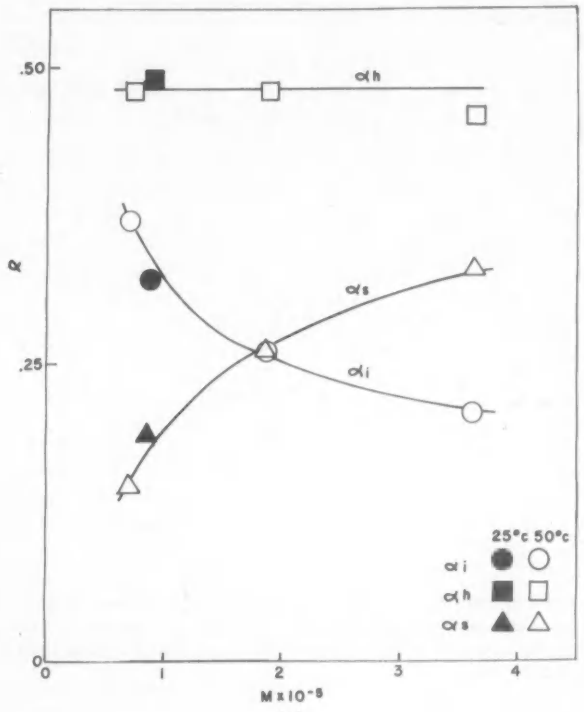
Tacticity and Molecular Weight of Polymer Prepared from Barium Methacrylate Dihydrate

The results of tacticity and viscosity-average molecular weight measurements on methylated samples of polymer prepared from barium methacrylate dihydrate are listed in Table III. Tacticity was determined by

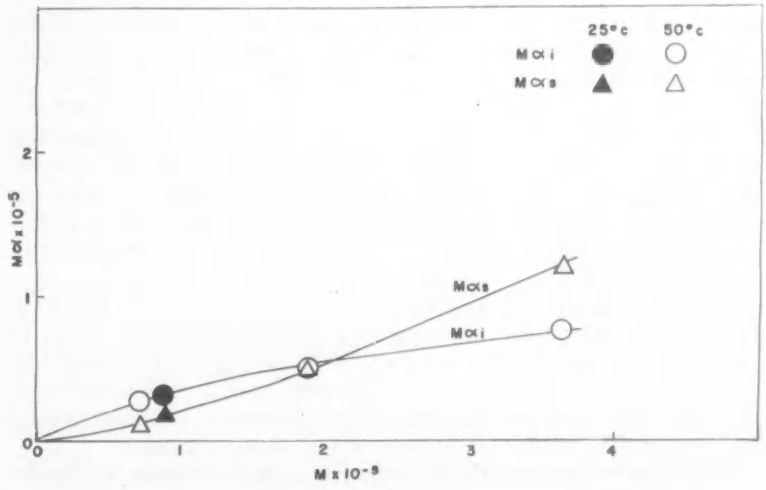
TABLE III
Characterization of Poly(Methyl Methacrylate) Derived from Polymerized Barium Methacrylate Dihydrate

Polymerization conditions						
Temp., °C.	Time, hr.	Conversion, (wt.-%)	$\bar{M} \times 10^{-5}$	α_i	α_h	α_s
120	66.5	53		0.49	0.43	0.08
101	91.1	44	1.60	0.49	0.41	0.10
73	66.8	59	1.39	0.36	0.48	0.16
50	63.6	9.4	0.72	0.37	0.48	0.15
50	110.1	19.4	1.88	0.26	0.48	0.26
50	162.0	58	3.64	0.21	0.46	0.33
25.5	670.4	3.6	0.89	0.32	0.49	0.19

interpretation of the high resolution nuclear magnetic resonance spectra in 15% chloroform solution by the method of Bovey and Tiers.[11] Viscosity-average molecular weights were determined from viscosity measurements in chloroform at 30°C. by using the correlations of Goode et al.[12]



(*a*)



(*b*)

Fig. 2. Polymerization of barium methacrylate dihydrate. Change of tacticity with chain length.

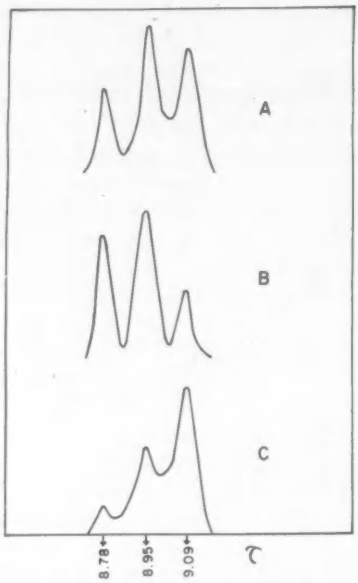


Fig. 3. NMR Spectra of poly(methyl methacrylate) of different origin: (*A*) barium methacrylate dihydrate, polymerized at 50°C., high conversion; (*B*) same, low conversion; (*C*) poly(methacrylic acid) prepared by free-radical polymerization in butanone solution at 60°C.

It can be seen from Table III that the tacticity of polymer produced at 25.5°C. and 50°C. is rather close to that corresponding to a random distribution of the configurations of asymmetric centers along the chain backbone (i.e. $\alpha_i = 0.25$, $\alpha_h = 0.50$, $\alpha_s = 0.25$). This is in marked contrast to the tendency of methacrylic acid to favor the formation of syndiotactic triads when polymerized in the liquid state.[8,13] Increasing polymerization temperature of barium methacrylate dihydrate leads, for similar monomer conversions, to a sharp increase in the frequency of isotactic triads.

The data in Table III also indicate that the molecular weight is proportional to yield at 50°C., as has been reported in the solid-state polymerization of acrylamide.[9]

The most striking result shown in Table III is the dependence of the tacticity on molecular weight for polymers produced below 50°C. That this dependence appears to be the same at 25.5°C. as at 50°C. is demonstrated in Figures 2*a* and 2*b*. The slope of the plots of $M\alpha_i$ or $M\alpha_s$ against M shown in Figure 2*b* gives the probability of information, at the corresponding reaction time, of either an isotactic or a syndiotactic triad.

Figure 3 directly compares the region in the NMR spectra corresponding to the α-methyl groups of polymer prepared from barium methacrylate dihydrate in the solid state at 50°C. (high and low conversion) with that

of polymer prepared from methacrylic acid in butanone solution at 60°C. (AIN initiator).[13]

Electron Spin Resonance Measurements on Irradiated Barium Methacrylate Dihydrate

Since the ESR spectrometer on which the measurements were carried out was not calibrated, no quantitative determination of radical concentrations could be made. However, a comparison of the ESR spectrum after irradiation but before polymerization with the spectrum after polymerization for 28 days at 50°C. is shown in Figure 4. Before polymerization

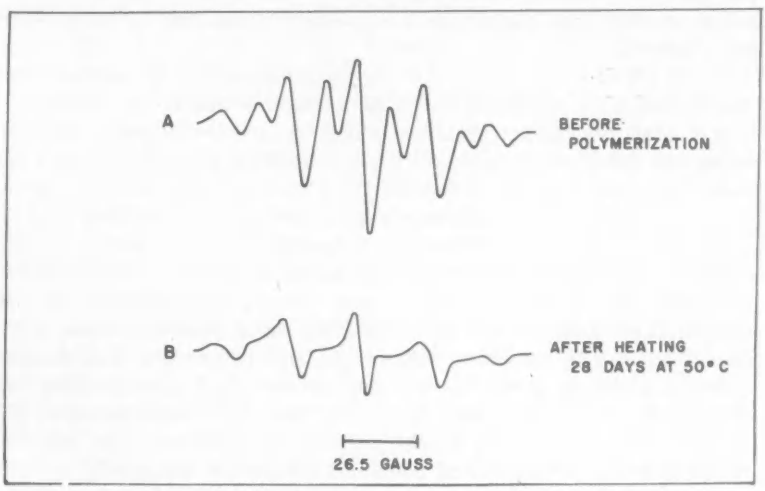


Fig. 4. ESR spectra of irradiated barium methacrylate dihydrate (dose 0.8 Mrad at −78°C.).

the characteristic nine line spectrum of the methacrylate radical[14] is present. After polymerization one can see that four of the lines have completely disappeared while the remaining five line spectrum is reduced relatively little in intensity. Bresler et al.[15] have associated the five line methacrylate spectrum with trapped radicals and the four line spectrum with that of the growing chain. Using this interpretation we should conclude that at the beginning of the solid state reaction both trapped and growing radicals are present while after polymerization at 50°C. for 28 days only trapped radicals remain.

III. DISCUSSION

The wide variation in the polymerizability of the salts of calcium acrylate and barium methacrylate can only be explained by assuming that the difference in the steric disposition of the reactive double bond is the governing

factor. Given this fact of crystal lattice control the question arises as to the extent to which the polymer chain grows within the crystal lattice. In this connection it is important to note that the crystallographic data on partially polymerized single crystals of both calcium acrylate dihydrate and barium methacrylate dihydrate indicate no change in the atomic positions of the remaining monomer. This implies that the chains grow at the surface of monomer crystallites and that they do not subject them to anisotropic strains sufficient to perturb systematically the atomic positions within the lattice. The picture of the growing chain that emerges is one of a growing end embedded in crystalline monomer with the rest of the polymer chain forming a separate phase. The likelihood of such a mechanism, proposed previously,[9] has been greatly strengthened by the present investigation.

It was noted previously[9,16] that the initiating species in radiation induced solid state polymerization is likely to be a radical-ion, which can lead to chain propagation by either radical or ionic mechanisms. Since in either case the growing chains will have a radical at one end and since bimolecular chain termination is unlikely in the solid state, an ESR signal is by itself no proof of a radical polymerization mechanism. However, in the case of the polymerization of barium methacrylate dihydrate at 50°C., we have some indication from the qualitative change in the nature of the ESR signal during the polymerization that chain growth takes place at the chain end carrying the radical. The ESR signal observed before polymerization may be associated with the presence of both free and trapped radicals, while the spectrum found after prolonged polymerization is characteristic of trapped radicals alone.[15] The virtual termination of the reaction after long periods of time can then be associated with the self-trapping of the growing radical in an area depleted of monomer.

Since the crystal lattice has been shown to determine the extent of the polymerization reaction it could also, in principle, determine the steric configuration of the polymeric product.

In calcium acrylate dihydrate the reactive double bonds have been shown to lie in narrow sections sufficiently far apart to preclude reaction between sections. Within a given section it would appear from Figures 1*a* and 1*b* that the growing end of the chain can attack at any time several monomer units of different orientation so that a high degree of stereoregulation would not be expected. Since barium methacrylate dihydrate has an arrangement similar to calcium acrylate and the identical crystal symmetry, the same argument should hold in that case.

The NMR measurements on poly(methyl methacrylate) prepared from barium methacrylate dihydrate after solid-state polymerization at 25.5° and 50°C. show that these polymers have an almost random sequence of configurations of the asymmetric centers. This suggests that the energetic advantage favoring syndiotactic growth in the liquid state is eliminated by the constraint imposed by the crystal lattice. It may be noted that the

tacticity of the polymerization product of crystalline methacrylic acid[8] is similar to that which we have now found for poly(barium methacrylate). The question then arises whether the characteristic differences in the tacticity of these polymers and of poly(methacrylic acid) prepared in the liquid state, will be encountered generally in solid-state polymerization of methacrylic acid derivatives, or whether they are associated specifically with certain crystal structures. This problem will be the subject of further investigations.

A strong argument in favor of a specific influence of the monomer crystal structure is the variation in the tacticity with the chain length of the polymer produced from barium methacrylate dihydrate at 25.5 and 50°C. This variation may be associated with the progressive disruption of the monomer lattice during the polymerization. From the slopes to the curves shown in Figure 2*b* we find that for chains which have grown to $\bar{M} = 7.2 \times 10^4$ the instantaneous effective values of triad formation probabilities are $\alpha_s = 0.24$, $\alpha_i = 0.29$, and $\alpha_h = 0.47$. When the chain attains $\bar{M} = 3.6 \times 10^5$, these values shift to $\alpha_s = 0.45$, $\alpha_i = 0.10$ and $\alpha_h = 0.55$. These values should be compared with $\alpha_s = 0.57$, $\alpha_i = 0.10$, and $\alpha_h = 0.33$ for methacrylic acid polymerized in solution.[13] We see then that the polymer prepared in the crystalline state becomes more syndiotactic with increasing chain length, approaching the tacticity of polymer prepared in a disordered phase.

The formation of isotactic placements has been shown to have a somewhat higher activation energy than syndiotactic growth in liquid state polymerization.[17] Nevertheless, the sharp increase in α_i when the polymerization temperature is above 100°C. exceeds by far the temperature dependence of the tacticity of polymers prepared in solution. It seems probable that the change in the stereochemistry of the polymer obtained at the higher temperatures is associated with the dehydration of the monomer. Since the anhydrous material does not polymerize to an appreciable extent, the polymerization would seem to take place during the monomer phase transition.

It would be expected that the polymerizability and the nature of the reaction product would be sensitive only to short-range order in the neighborhood of the growing chain end. Thus, materials which appear disordered by the criterion of x-ray diffraction may still be characterized by short-range order affecting a chemical reaction. This point is illustrated in a striking manner by the large difference in the reactivity of the amorphous calcium acrylate derived from the monohydrate and the dihydrate respectively. It is significant that the product originating from the reactive dihydrate polymerized faster than that which was prepared from the inert monohydrate. Such a "memory effect" has been described previously for inorganic amorphous solids,[18] but this seems to be the first instance of an analogous phenomenon in an organic reaction.

IV. EXPERIMENTAL

Monomer Preparation and Characterization

In the preparation of barium methacrylate dihydrate and calcium acrylate dihydrate the solid hydroxide was added with stirring to an approximately 3*N* water solution of freshly distilled acrylic or methacrylic acid. At the phenolphthalein endpoint a slight excess of acid was added and the solution was filtered to remove any undissolved material. The salts were crystallized from the water solution by slow evaporation at room temperature and stored in a desiccator over a saturated solution of calcium chloride. These salts dehydrate between 50 and 100°C.

Anhydrous barium methacrylate and calcium acrylate monohydrate were prepared by dissolving the corresponding dihydrates in hot methanol and recrystallizing by cooling. These salts were stored in a desiccator over Drierite. Calcium acrylate monohydrate also dehydrates between 50 and 100°C.

The two anhydrous crystalline forms of calcium acrylate were prepared by heating the dihydrate or the monohydrate in a sealed container at 101°C. for a period of about four days. These salts were stored in a desiccator over P_2O_5.

"Amorphous" anhydrous calcium acrylate was prepared by dehydration of the dihydrate or the monohydrate in a desiccator containing P_2O_5 at a pressure of 0.01 mm. Hg for 24 hr. at room temperature. The resulting salts were stored in a desiccator over P_2O_5.

None of the anhydrous salts melted or decomposed below 200°C.

The composition of the barium salts was determined gravimetrically by precipitating barium in the form of its sulfate. The composition of the calcium salts was determined by titration with ethylenediaminetetraacetic acid in basic solution with Murexide as the indicator.[19]

Polymerization

From 1.5 to 5 g. of finely ground samples of monomer were sealed in the atmosphere in 11 mm. Pyrex tubing. The tubes were then packed in a Dewar flask filled with Dry Ice, and were exposed to a gamma radiation dose of 0.8 Mrad from a Co^{60} source. After removal from the radiation source, the samples were placed in constant temperature baths to start a kinetic run. The extent of polymerization was determined at various times by extracting the residual monomer from a sample tube with water containing a small amount of hydroquinone, filtering off the polymer, washing with water, drying at 100°C. for at least 8 hr., and weighing.

X-Ray Diffraction

All x-ray powder data were obtained with CuKα radiation. An automatic recording Philips diffractometer was used to determine x-ray diffraction peaks of the barium salts in the 2θ range from 4° to 60°. The x-

ray diffraction peaks of the calcium salts were determined from Debye-Scherrer x-ray powder photographs. The cameras used had a radius of 57.3 mm. and employed a Straumanis-type film arrangement.

Single-crystal x-ray diffraction data for calcium acrylate dihydrate were obtained for the $h0l$, $h1l$ and $0kl$ planes of reciprocal space. Photographs of the $h0l$ and $h1l$ plane were taken with an equi-inclination Weissenberg camera using CuKα radiation. Data from the $hk0$ plane of reciprocal space were taken with a precession camera using MoKα radiation. Weissenberg photographs of the $h0l$ plane of a partially polymerized single crystal of calcium acrylate dihydrate were taken with the same crystal used for the data on the pure monomer.

Single-crystal x-ray diffraction data for barium methacrylate dihydrate for the $hk0$, $0kl$, and $1kl$ planes of reciprocal space were taken with a precession camera using MoKα radiation. The same crystal used above was polymerized and precession pictures were taken for the $hk0$ and $0kl$ planes of the partially polymerized crystal.

Nuclear Magnetic Resonance and Viscometry

NMR spectra and viscometry data were taken on poly(methyl methacrylate) derived from the poly(barium methacrylate). NMR spectra were taken on a 15% chloroform solution of the poly(methyl methacrylate) samples sealed in an NMR tube at a temperature of approximately 90°C. The instrument used was a Varian 4300C H.R. 60 Mcycle/sec. NMR spectrometer. Viscometry data were taken with an Ubbelohde dilution viscometer at 30°C. on chloroform solutions of the poly(methyl methacrylate) samples in the concentration range of 0.1–0.7 g./100 ml.

To convert poly(barium methacrylate) to poly(methyl methacrylate) the polymeric salt was dissolved in slightly acidified methanol, poly(methacrylic acid) was precipitated by the addition of 6N HCl and the polyacid was methylated by the addition of a benzene solution of diazomethane prepared from nitrosomethylurea.[20] The polymer was then precipitated from benzene solution by the addition of heptane and dried under vacuum.

Electron Spin Resonance Measurements

Finely powdered barium methacrylate dihydrate was irradiated in the manner previously described. After irradiation, two melting point tubes of 2 mm. inner diameter were packed with monomer and sealed. One tube was placed in a Dewar flask filled with Dry Ice and the other in a 50°C. constant temperature bath for 28 days. At this time ESR spectra were taken of each tube at room temperature. The ESR spectra were recorded by Mr. Michael Kaplan of Columbia University using a superheterodyne X-band spectrometer with reflection cavity, operating with a field of 3000 gauss and a modulation amplitude of 2.5 gauss.

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Synopsis

Different crystalline and amorphous modifications of calcium acrylate in anhydrous and hydrated form and barium methacrylate dihydrate were irradiated at −78°C. with gamma rays and their post-polymerization at 50° and 100°C. was studied. With calcium acrylate the anhydrous crystalline salt and the dihydrate could be polymerized while the monohydrate was inert. Two different crystalline modifications of the anhydrous salt behaved quite differently, and the polymerization rate of the anhydrous amorphous salt depended on the hydrate form from which it originated. The crystal structure of calcium acrylate dihydrate was determined and it showed that the reactive double bonds lie in sections of 3 A. thickness, separated from each other by a distance of 7 A. The polymerization of barium methacrylate dihydrate led to a polymer which was much less syndiotactic than poly(methacrylic acid) prepared in solution. The tacticity of this polymer depended markedly on the molecular weight at 25.5 and 50°C., presumably because the restraints imposed by the crystal lattice of the monomer are decreasing during the polymerization. The molecular weight of the polymer obtained at 50°C. was proportional to the monomer conversion. A preliminary crystallographic analysis indicates that barium methacrylate dihydrate has a structure similar to that of calcium acrylate dihydrate.

Résumé

On a irradié à −78°C au moyen de rayons-gamma différentes formes cristallines et amorphes d'acrylate de calcium anhydride et hydraté ainsi que du méthacrylate de barium dihydrate; on a étudié leur postpolymérisation à 50° et 100°C. Avec l'acrylate de calcium on peut polymériser le sel cristallin anhydre et le dihyrate alors que le monohydrate est inerte. Deux formes cristallines différentes du sel anhydre se comportent de façon fort différente et la vitesse de polymérisation du sel amorphe anhydre dépend de la forme hydratée dont il provient. On a déterminé la structure cristalline

de l'acrylate de calcium dihydrate et on montre que les doubles liaisons réactionnelles se trouvent en sections de 3 A. d'épaisseur, séparés par une distance de 7 A. La polymérisation du méthacrylate de barium d'hydrate conduit à un polymère qui est beacoup moins syndiotactique que l'acide polyméthacrylique préparé en solution. La tacticité de ce polymère dépend nettement du poids moléculaire à 25.5 et 50°C; on présume que les restrictions imposées par le réseau cristallin du monomère diminuent pendant la polymérisation. Le poids moléculaire du polymère obtenu à 50°C est proportional au taux de conversion du monomère. Une analyse cristallographique préliminaire indique que le méthacrylate de barium dihydraté a une structure semblable à celle de l'acrylate de calcium dihydraté.

Zusammenfassung

Verschiedene kristalline und amorphe Modifikationen von wasserfreiem und Hydratwasser enthaltendem Calciumacrylat sowie Barium-methacrylat-Dihydrat wurden bei −78°C mit γ-Strahlen bestrahlt und ihre Nachpolymerisation bei 50° und 100°C untersucht. Im Falle des Calciumacrylats konnten das wasserfreie kristalline Salz und das Dihydrat polymerisiert werden, während das Monohydrat nicht reagierte. Zwei verschiedene Modifikationen des wasserfreien Salzes verhielten sich ganz verschieden und die Polymerisationsgeschwindigkeit des wasserfreien amorphen Salzes war davon abhängig, aus welcher Hydratform es hergestellt wurde. Es wurde die Kristallstruktur von Calciumacrylat-Dihydrat untersucht und gefunden, dass die reaktionsfähigen Doppelbindungen innerhalb von Abschnitten liegen, deren Dicke 3 A. und deren gegenseitiger Abstand 7 A. ist. Das bei der Polymerisation von Bariummethacrylat-Dihydrat gebildete Polymere wies eine viel geringere Syndiotaktizität als in Lösung hergestellte Polymethacrylsäure auf. Die deutliche Abhängigkeit der Taktizität des bei 25,5 und 50°C hergestellten Polymeren vom Molekulargewicht geht vermutlich darauf zurück, dass die durch das Kristallgitter des Monomeren erzwungene Ordnung während der Polymerisation abnimmt. Das Molekulargewicht des bei 50°C gebildeten Polymeren ist dem Monomerumsatz proportional. Nach einer vorläufigen kristallographischen Analyse ist die Struktur von Bariummethacrylat-Dihydrat derjenigen von Calciumacrylat-Dihydrat ähnlich.

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Polymerization in the Crystalline State. V. Oriented Chain Growth in the Thermally Initiated Polymerization of *p*-Acetamidostyrene and *p*-Benzamidostyrene*

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INTRODUCTION

In previous papers of this series[1–4] it was pointed out that the central problem in the study of polymerizations in the crystalline state is the assessment of the role played by the geometric disposition of the monomer molecules in the crystal lattice in determining the characteristics of the reaction. A number of observations led us to the conclusion that the geometric factors are of crucial importance—most convincingly, perhaps, the finding that the solid state polymerizabilities of different salts of acrylic acid[2] or of different crystalline and amorphous modifications of calcium acrylate[4] vary widely from each other. However, in no previous study of vinyl polymerization in the crystalline state was the polymer chain observed to grow in a crystallographic direction of the monomer. This was, in fact, one of the reasons why the role of the monomer crystal lattice in solid-state polymerization processes was at one time questioned.[5] The widespread belief that the polymer formed in solid-state vinyl polymerizations is isotropic, led also to the assumption that the residual birefringence of a monomer crystal is proportional to the fraction of the monomer which has not polymerized.[6,7]

On the other hand, for the polymerization of some cyclic monomers clear evidence has been offered that growth of the polymer chains may be directed in a crystallographic direction of the monomer. More than thirty years ago Kohlschütter demonstrated that contact of formaldehyde vapor with trioxane crystals leads to the formation of polyoxymethylene chains oriented in the direction of the *c* axis of the hexagonal trioxane.[8] It is surprising that this spectacular finding does not seem to have met at the time with any appreciable interest on the part of scientific community—so

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that it was forgotten when problems of solid-state polymerization began to be investigated in a systematic manner during the past ten years. More recently, Okamura and his associates demonstrated that the structure of the monomer lattice imposes an orientation on polymers obtained by gamma irradiation of trioxane, β-propiolactone, diketene, and 3,3-bischloromethylcycloxabutane.[9] In the case of the polyoxymethylene obtained by the post-polymerization of irradiated large crystals of trioxane, the polymer was found to be highly ordered not only with respect to the orientation of the fiber axis, but also in the manner in which the polymer chains were packed, so that the material resembled in its x-ray diffraction behavior a large single polymer crystal.[10,11]

In the present study we have shown that oriented chain growth is also possible in the solid-state polymerization of some vinyl monomers. Indications of this phenomenon were observed with *p*-acetamidostyrene (AAS) and were studied in much greater detail on *p*-benzamidostyrene (BAS). Both these monomers polymerize spontaneously at temperatures far below their melting point.

RESULTS

Polymerization Kinetics

The fact that AAS polymerizes spontaneously below its melting point of 147°C. was mentioned in a footnote of a paper published in 1956 by Hahn and Fischer.[12] We have confirmed their finding and have been able to follow the kinetics of the polymerization process by infrared spectroscopy at temperatures as low as 97.8°C. The results are plotted in Figure 1, which shows that the polymerization proceeds at a constant rate in its initial stages without any indications of an induction period. At higher

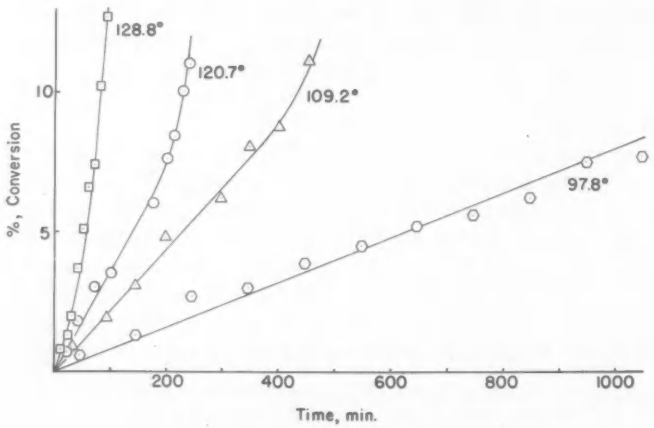


Fig. 1. Polymerization kinetics of AAS crystals.

conversions there seems to be a tendency for the polymerization rate to accelerate. The overall activation energy corresponding to the initial rates was 18 kcal./mole. Polymerization of AAS in the liquid state was studied in mixtures with acetanilide containing 47 mole-% AAS. The results are

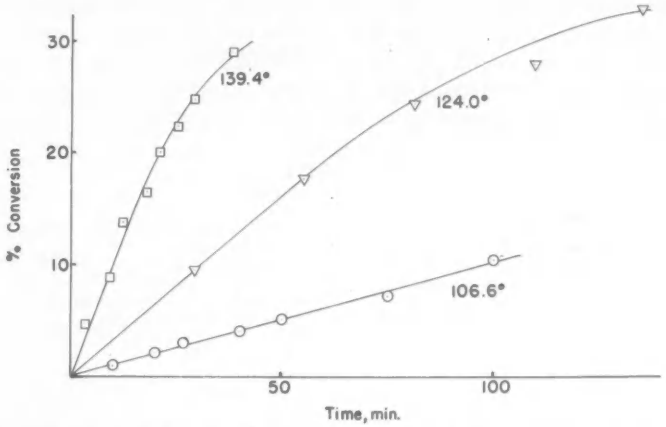


Fig. 2. Polymerization kinetics of AAS in the liquid state (acetanilide diluent, 47 mole-% AAS).

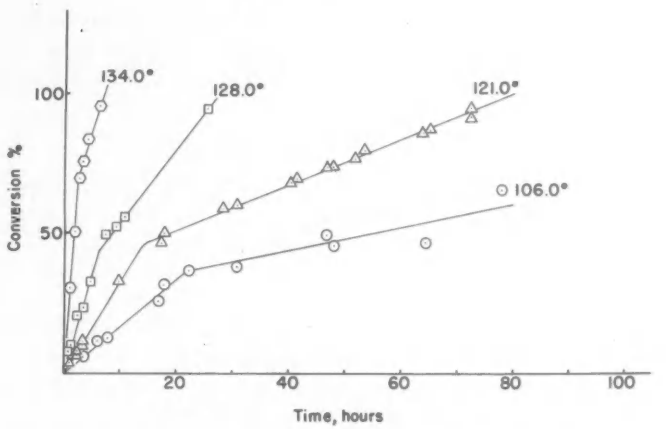


Fig. 3. Polymerization kinetics of BAS single crystals.

plotted in Figure 2. In spite of the monomer dilution, the initial polymerization rate was 5 to 6 times higher than that of the crystals at comparable temperatures. The activation energy, 21 kcal./mole, was slightly higher than that observed with crystalline AAS. In contrast to the solid-state

reaction which tended to accelerate at higher monomer conversions, the rate of the reaction in the liquid tended to slow down.

The polymerization of BAS (m.p. 178°C.) was followed at temperatures as low as 104°C. This monomer has the advantage that it can be crystallized from triethyl orthoformate in the form of thin flakes of very uniform thickness, so that the extent of conversion can be followed by infrared spectroscopy both on microcrystalline samples and on single crystals. The kinetic curves are shown in Figure 3; they illustrate the general observation that the polymerization proceeded at a constant rate up to a critical conversion, when it slowed down, rather abruptly, to a lower constant rate.

TABLE I
Kinetics of BAS Polymerization

Temp., °C.	Polymerization rate, %/min.		Critical conversion, %
	Slow stage	Fast stage	
107	0.014	0.007	16
126	0.1	0.05	22
135	2.3	1.5	27
148	4.8	2.2	62
157	20	6.0	73

The zero-order rate constants in the "fast" and "slow" stage as well as the critical conversions at which the rate passed from one value to the other are listed in Table I. It may be seen that the critical conversion increased with rising temperature. An Arrhenius plot of the initial rates is shown in Figure 4. It corresponds to an activation energy of 42 kcal./mole. It

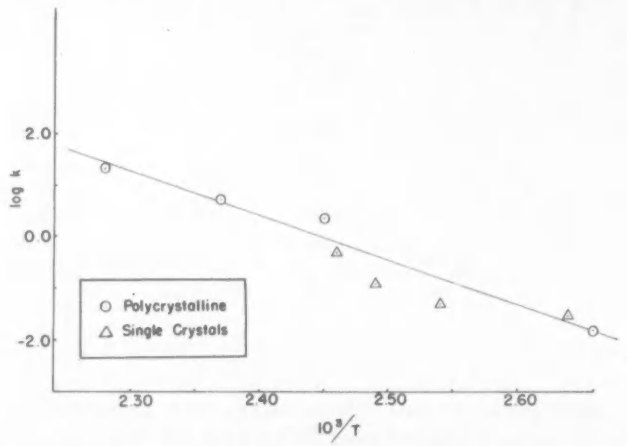


Fig. 4. Arrhenius plot of the initial polymerization rate of BAS crystals: (○) microcrystalline samples; (△) large single crystals.

should be noted that rates measured on large single crystals differed only slightly from those observed with microcrystalline samples.

The effect of preirradiation with gamma rays from a Co^{60} source on the polymerization rate was investigated with AAS. It was found that the initial rates at 85, 100, and 110°C. were increased by less than a factor of two over the rates to be expected with unirradiated samples.

Volumetric Measurements

The densities at 25°C. as well as the thermal coefficients of expansion in the range of 0°C. to 70°C. are listed for AAD, BAS and their polymers in Table II. It may be noted that both AAS and BAS expand on polymeri-

TABLE II
Densities and Coefficients of Expansion of Monomers and Polymers

	d_{20}, g./cc.	$10^4\alpha$
AAS	1.176	2.0
Poly-AAS	1.165	2.3
BAS	1.250	1.4
Poly-BAS	1.217	1.9

zation. Moreover, since the polymers have the higher thermal coefficients of expansion, the increase in volume on polymerization will be even higher at the temperatures at which polymerization proceeds at an observable rate than at 25°C. For AAS, polymerization increases the volume at 100°C. by 1.2%, for BAS the increase amounts to 2.2%.

Dilatometric studies of the polymers indicated for poly-AAS a glass transition temperature $T_g = 85$°C., while for poly-BAS $T_g = 120$°C.

Characterization of Monomer Crystals

Crystals of AAS are orthorhombic, space group *Pbca*, with $a = 7.05$ A., $b = 9.7$ A., and $c = 25.5$ A. The unit cell contains eight molecules. These data are strikingly similar to the crystal structure of acetanilide,[13] which belongs to the same space group and has unit cell dimensions $a = 7.98$ A., $= 0.48$ A., $c = 19.64$ A. The difference in the dimension of the c axis of acetanilide and *p*-acetamidostyrene is just sufficient to accommodate the vinyl groups; the smaller value of a axis in AAS is probably due to a smaller angle between the plane of the aromatic ring and the 100 plane. A tentative crystal structure for AAS based on the analogy with acetanilide is shown in Figure 5. It may be seen that the monomer molecules are arranged in hydrogen-bonded chains with a twofold screw axis. The reactive vinyl groups lie in sheets perpendicular to the c axis which are separated from each other by a distance of over 10 A. It should be noted that the molecules point alternately to either side of the sheet containing the vinyl groups. When AAS is crystallized from ethyl acetate, the crystals form as thin platelets whose large face is perpendicular

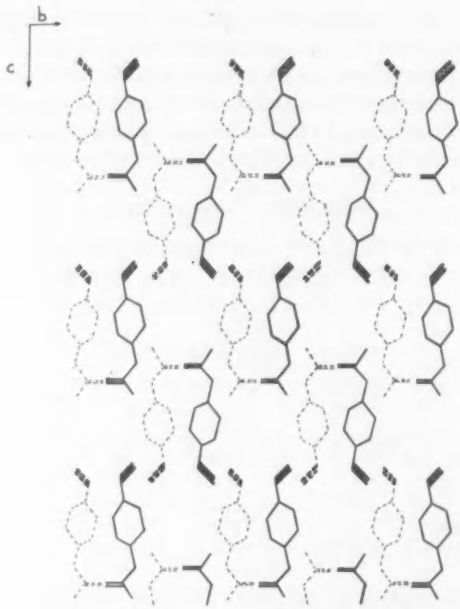


Fig. 5. Probable crystal structure of AAS.

to the crystallographic c axis. The refractive index is $n = 1.627$ for light polarized in the b–c plane and $n = 1.492$ for light polarized in the a–c plane.

Crystals of BAS obtained from triethyl orthoformate were thin flakes, 2–10μ thick. Analysis of x-ray diffraction data showed that the crystal is orthorhombic, space group $Ima2$, $a = 8.04$ A., $b = 5.3$ A., $c = 28.0$ A., with four molecules per unit cell. The probable arrangement of the monomer molecules in the crystal lattice is shown in Figures 6a and 6b. The monomers occur again in hydrogen-bonded chains, but in contrast to the arrangement in the AAS crystal, the BAS molecules in these chains are all oriented in the same direction. The reactive double bonds lie in sheets perpendicular to the c axis and separated from one another by spacings of 14 A. The large face of the crystal flakes is perpendicular to c; the refractive indices are $n = 1.560$ for light polarized in the a–c plane and $n = 1.670$ for light polarized in the b–c plane.

The projection of the N—H bonds onto the a–b plane is parallel to b as may be confirmed from observations of the infrared dichroism in a single crystal. The absorption band at 3340 cm.$^{-1}$, corresponding to the N—H stretching vibration is observed when the radiation is polarized in the b–c plane, but is absent when it is polarized in the a–c plane. It may be noted that the C—H out-of-plane bending vibration band at 993 cm.$^{-1}$ would be expected to be inactive with radiation polarized in the b–c plane, if the

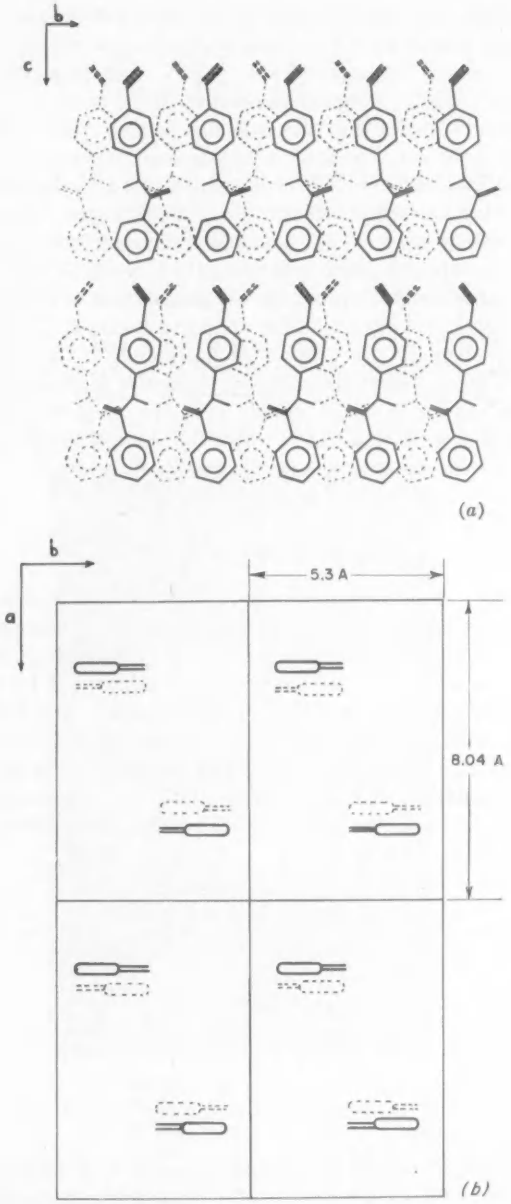
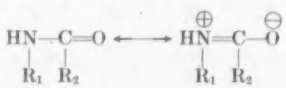


Fig. 6. Probable crystal structure of BAS: (*a*) projection on *b*–*c* plane; (*b*) projection on *a*–*b* plane. (The molecules on the lower level represented by dashed lines are shifted to render them visible.)

vinyl group were coplanar with the H—N—C=O structure. Because of the well known resonance



the entire BAS molecule should form a single conjugated structure and lie in a plane. However, the dichroic ratio of the 993 cm.$^{-1}$ band was found to be only ~0.6, corresponding to an angle of ~36° between the plane of the vinyl groups and the plane defined by the HN—C=O grouping. Distortions of conjugated structures from coplanarity due to the intermolecular forces operating in the crystal lattice are quite common. They have been described, for instance, on crystals of acetanilide.[13] A difficulty arises because space group *Ima*2 with only four molecules per unit cell requires the molecules to have a plane of symmetry. We must conclude that the crystal consists of small domains in which the plane of the styryl residues is twisted in alternate directions from the plane defined by the amide groupings.

Characterization of Polymers

The infrared spectra of the polymers were similar to those of the parent monomer except for the absence of absorption bands characteristic of the vinyl groups and a general broadening such as is commonly observed with macromolecules. The chain lengths were characterized by solution viscosity measurements in pyridine solution at 25°C. Intrinsic viscosities of poly-AAS obtained by carrying the polymerization of the monomer crystals to various degrees of conversion over a range of temperatures with or without preirradiation are listed in Table III. The following points should be noted: (*a*) the intrinsic viscosities indicate that the chains are very long,

TABLE III
Intrinsic Viscosities of Poly-AAS

Preirradiation dose, Mrad	Polymerization Temp., °C.	Monomer conversion, %	[η], dl./g.
0	120	1.6	0.740
0	120	5.5	0.968
0	120	79.0	0.790
0	100	1.8	0.478
0	100	2.8	0.395
0	100	20.0	0.310
1	120	16.2	1.018
1	120	28.2	1.348
1	120	100.0	0.810
1	100	6.4	0.360
1	100	27.1	0.383
1	100	47.0	0.360

but there is no significant dependence of chain length on monomer conversion; (*b*) the polymer chain length seems to be the same, whether or not the polymerizing crystals had been preirradiated.; (*c*) intrinsic viscosities of polymers prepared at 100°C. are distinctly lower than of those prepared at 120°C. With poly-BAS at full monomer conversion, the reduced viscosities were very low and increased with dilution of the solution in a manner which allowed no valid extrapolation. The results may be exemplified by the specific viscosities of 0.048 and 0.071 in solutions containing 1 g./100 ml. of polymer prepared at 110 and 130°C., respectively.

Microscopic Observation of Polymerizing Single Crystals

A single crystal of AAS about 1 mm. long, 0.7 mm. wide and 0.02 mm. thick was observed under the polarizing microscope after heating at 120°C. for various periods of time. It was found that an optically isotropic phase was forming at the edges of the crystal and advancing inward, the rate of

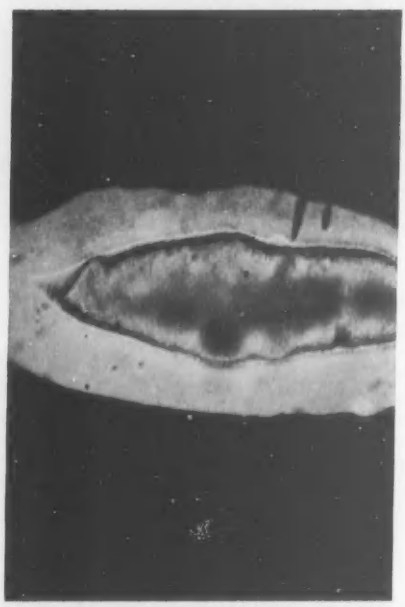


Fig. 7. Appearance of a partially polymerized AAS single crystal under the polarizing microscope (heating time 3 hr. at 120°C.).

advance being much greater in the *c* direction than the *b* direction. The remaining lens-shaped birefringent area, whose anisotropy was unchanged, was divided sharply by a phase boundary as shown on Figure 7. The outer and inner phase boundary of the birefringent region advanced at equal rates during the reaction. With some crystals which had a terraced

surface, the changes in the appearance of the interference pattern suggested that polymerization was taking place in successive thin layers of the crystal with the reaction proceeding concentrically from the outer edges of the crystal towards the center.

The behavior of single crystals of BAS depended on whether they were heated above or below 120°C., the glass transition temperature of the polymer. Above that temperature, the interference colors observed under the polarizing microscope changed uniformly over the entire area of the crystal until all birefringence disappeared. Below T_g, there was almost no change in the birefringence of the specimen even in cases where an examination of the infrared spectrum revealed that polymerization had converted more than 60% of the monomer.

Infrared Dichroism

Changes in the dichroism of the absorption band at 3340 cm.$^{-1}$ corresponding to the N—H stretching vibration were followed in heated BAS single crystals concurrently with the absorption of the 993 cm.$^{-1}$ band due to C—H out-of-plane vibrations in the vinyl residues. It was found that in crystals polymerizing above 120°C., the dichroism decayed at a rate to be expected on the assumption that the polymer formed is isotropic. However, in crystals polymerizing below 120°C., the dichroism remained unchanged even with 80% of the BAS converted to polymer. In a run

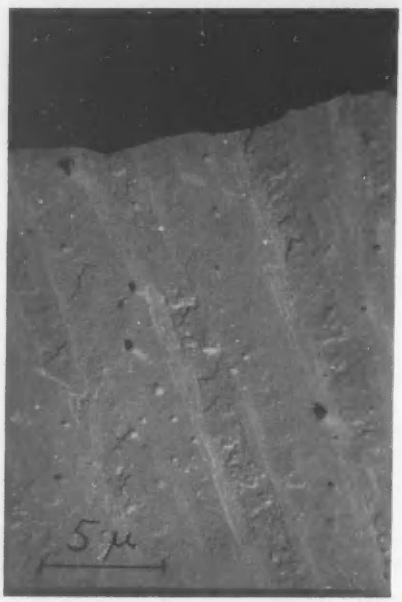


Fig. 8. Surface of an unheated BAS crystal.

carried out at 121°C., it was found that the optical density at 3340 cm.$^{-1}$ in light polarized in the b–c plane was linear in time and did not show the break characterizing the monomer conversion-time plot.

Electron Microscopy

The results of electron microscopic studies of the surface of BAS crystals before and during thermally initiated polarization are shown in Figures

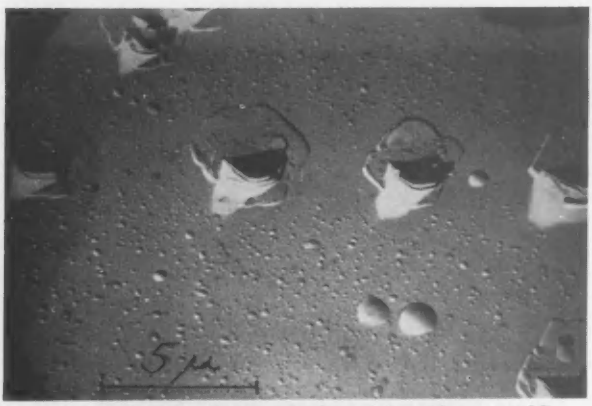


Fig. 9. Surface of a BAS crystal heated for 10 hr. at 110°C.

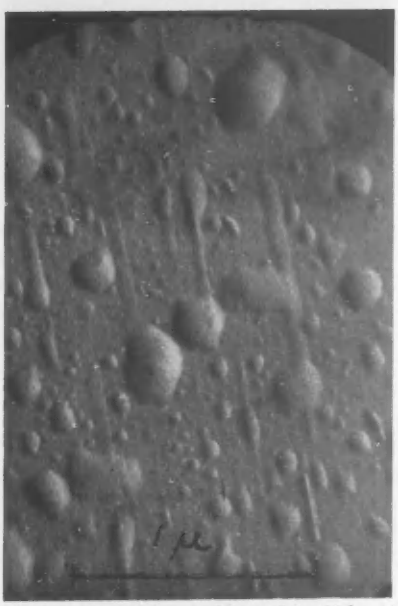


Fig. 10. Surface of a BAS crystal heated for 25 hr. at 110°C.

8–11. The surface of the unheated crystal (Fig. 8) is rather flat with characteristic ridges. Heating at 110°C., below the glass transition temperature, produced striking changes. In Figure 9 we may observe hexagonal protrusions from which leaflike flakes seem to be peeling off in a manner suggesting the pages of an opening book. In Figure 10, the surface character of the crystal is completely changed. It is significant that the protrusions seem to be oriented in some crystallographic direction. Finally,

Fig. 11. Surface of a BAS crystal heated for 2 hr. at 125°C.

in Figure 11, we see the surface of a crystal heated above T_g for a time corresponding to about 10% monomer conversion. The appearance of this surface suggests a film under tension attached in circular areas to the underlying structure. Note the regular array of the dark circles and the pattern of wrinkles suggesting the stressed condition of the surface layer.

DISCUSSION

The spontaneous polymerization of crystalline vinyl monomers have been reported previously for 4,4′-divinyldiphenyl[14] and for butadiene-1-carboxylic acid,[3] but in both cases the process was investigated only in a cursory manner. Our present results provide much more extensive information on the kinetics of thermally initiated vinyl polymerization in the crystalline state, and they furnish for the first time clear evidence that it is possible to utilize the directing influence of the crystal lattice geometry to obtain in

the polymerization of vinyl monomers oriented chain molecules. We shall now discuss in succession these two aspects of this investigation.

Kinetic Pattern

The usual criteria used to distinguish free-radical from ionic polymerizations are largely inapplicable to solid-state reactions, and it is in many cases not possible to classify the mechanism of a polymerization proceeding in the crystalline state.[15] Nevertheless, when the polymerization is initiated thermally, as in the present study, the conclusion is inescapable that a radical is the initiating species. The exact nature of the initiating process is in doubt and it is in particular not known whether surface oxidation of the crystal might not play a role—but this seems on the whole unlikely, since polymerization rates observed in air differed only slightly from those in samples which were heated in sealed evacuated tubes.

In an attempt to interpret the kinetic pattern the following observations should be considered. (*a*) The kinetic curves exhibit no induction period such as is typical of many solid-state reactions in which a new phase has to be nucleated.[16,17] (*b*) The polymerization rate of BAS is the same in relatively large single crystals and in ground microcrystalline samples. (*c*) Irradiation with a heavy dose of gamma rays has relatively little effect on the polymerization rate. (*d*) The polymer chain length is independent of monomer conversion and is similar in samples polymerized with or without irradiation. (*e*) An Arrhenius plot of initial rates of BAS polymerization shows no break at the glass transition temperature of the polymer. (*f*) The appearance of polymerizing crystals of AAS under the polarizing microscope shows clearly that the reaction cannot proceed in a direction perpendicular to the large surface of the crystal platelets. With AAS the reaction starts at the edge of the crystal while with BAS the thickness of the polymer layer appears to be uniform, at all stages of the reaction, over the entire area of the large crystal face. (*g*) Electron microscopy reveals deep-seated changes in the surface appearance of BAS crystals even at very low degrees of monomer conversion.

Since we know that the monomer crystal lattice has a layer structure with the reactive double bonds lying in sheets separated by very long distances, it seems safe to assume that only vinyl groups lying in any one of these sheets (in the crystallographic 001 planes) can participate in the formation of a single polymer chain. In the case of AAS, evidence for such directed growth comes from observations under the polarizing microscope, while evidence for BAS rests on measurements of infrared dichroism and electron microscopy to be discussed in the next section. We believe that polymerization can take place only on the crystal surface or at the monomer–polymer interface. With BAS, initiation takes place, apparently, on the 001 crystal face and chain propagation is rapid compared to the initiation process, so that essentially an entire layer of monomers is converted to polymer before the underlying layer is attacked. With AAS, initiation appears to be favored at a crystallographic face at the edge of the crystal

platelet and propagation takes place simultaneously in a number of 001 layers. Gamma irradiation cannot substantially increase the polymerization rate, since radicals in the body of the crystals cannot initiate polymerization. The small effect on the rate produced by the grinding of BAS crystals may be due to the fact that the dimensions of the platelets in the *c* direction are very small ($\sim 2\mu$) even in large single crystals and may not be altered substantially by the grinding operation, so that the total surface area of the 001 faces may be very similar in large crystals and microcrystalline samples. This picture also agrees with the zero-order kinetics observed particularly with BAS up to substantial degrees of conversion. The causes for the acceleration in the polymerization of AAS crystals at higher conversions and for the abrupt decrease in the polymerization rate of BAS are obscure.

In the case of AAS we have obtained comparative data for the polymerization rate of the monomer crystals and the rate in a liquid mixture of AAS and acetanilide. The reaction in the liquid state may be compared with the rate of the thermally initiated polymerization of styrene in the absence of oxygen studied many years ago by Schulz and Husemann.[18] They found the initial rate to be proportional to the square of the monomer concentration and if we assume the same relation to hold in our system, AAS is found to polymerize thermally about 8 times more slowly than styrene. The overall activation energy of 21 kcal./mole reported by Schulz and Husemann is very close to the value of 18 kcal./mole for liquid AAS and identical with the result obtained for AAS crystals. This close correspondence is surprising, since one might have expected chain initiation to require a higher activation energy when the monomer molecules are restrained by the forces of the crystal lattice. On the other hand, the overall activation energy for the polymerization of BAS crystals has the strikingly higher value of 42 kcal./mole. The enormous difference in the ΔE^* for the polymerization of AAS and BAS can clearly not be accounted for on chemical grounds and seems to reflect differences in the geometrical arrangement of the monomer molecules in their respective crystal lattices. It should be pointed out that the apparent activation energies for thermally initiated polymerizations contain a dominant contribution from the initiation process and should, therefore, not be compared with values obtained in radiation initiated processes, where this contribution is absent.

Oriented Growth of Polymer Chains

The appearance of partially polymerized single crystals of AAS under the polarizing microscope revealed clearly the existence of two anisotropic phases (see Fig. 7). This observation suggested that the monomer may first be converted to an oriented polymer, whose orientation is gradually lost by a relaxation process. A spectroscopic study of single crystals in polarized infrared light is particularly suitable for the investigation of the details of such a process. For this purpose BAS is on three counts much more suitable than AAS: (*a*) it forms crystal platelets of very uniform

thickness in a range corresponding to desired optical densities of some important absorption bands; (*b*) an absorption band corresponding to a chemical bond which is not altered by the polymerization reaction has an infinite dichroic ratio; (*c*) the BAS crystals have a much smaller vapor pressure than AAS, so that sublimation during extensive experiments at elevated temperatures is not a problem.

The results of the experiments described above leave no doubt that polymerization of BAS crystals below the glass transition temperature of its polymer leads to the formation of chains in which the orientation of the hydrogen-bonded structure characterizing the crystal lattice of the monomer remains unaltered. This conclusion is based mainly on the retention of the infrared dichroism during the polymerizations, but is supported also by the results of electron microscopy, the appearance of polymerized single crystals under the polarizing microscope and the kinetic pattern of the reaction. Since the Arrhenius plot of initial rates of BAS polymerization shows no break at T_g, it is concluded that an oriented polymer forms first even at higher temperatures, although its orientation may be rapidly lost by a relaxation process. This conclusion was reinforced by the results obtained when a single crystal was polymerized within 1°C. of T_g. In that case, the concurrent measurement of the dichroism due to N—H vibration and the disappearance of vinyl groups showed that the isotropic polymer was formed at a constant rate, although the rate of polymerization showed a break at a critical conversion. Since the reactive double bonds lie in sheets separated by very long distances, we need to consider only their arrangement in one such sheet in an attempt to define the geometric pat-

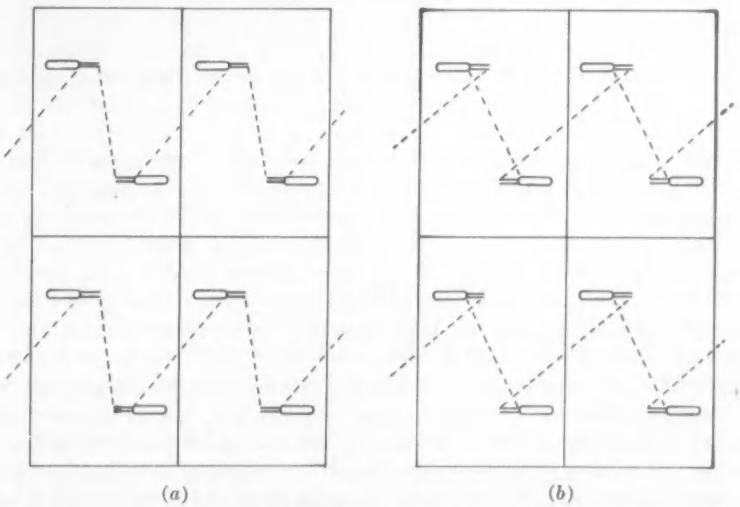


Fig. 12. Schematic representation of the polymerization of BAS: (*a*) Formation of *threo* head-to-head, tail-to-tail polymer; (*b*) formation of syndiotactic polymer.

tern of chain propagation. Inspection of Figure 6*b* shows that a chain growing in the crystallographic *b* direction could contain two monomer residues for a length of 5.3 A., and would thus have about the extension to be expected for an all-*trans* conformation of the backbone of a vinyl polymer. Growth in any other direction would involve much greater chain extension and seems, therefore, excluded. The *b* direction is also the direction of the hydrogen-bonded structure and a chain growing in this manner would have alternate substituents joined by intramolecular hydrogen bonds. It is envisaged in this interpretation that two sheets of hydrogen-bonded monomer molecules lying parallel to one another are joined by the

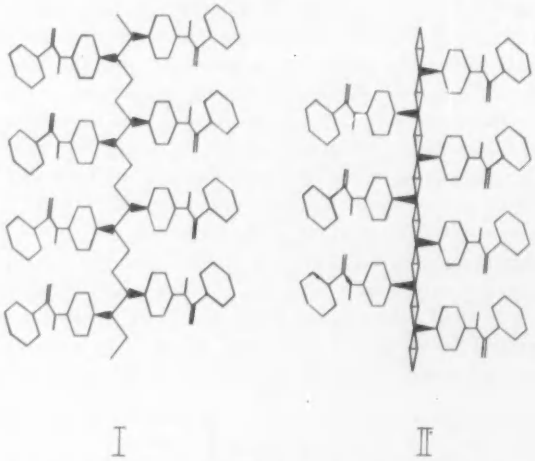


Fig. 13. Possible products of chain propagation in the direction of the *b* axis of the BAS crystal.

polymerization reaction. During this process, the hydrogen-bonded sheets of the chain substituents swing around the *b* axis so as to satisfy the tetrahedral bond requirement, but the orientation of the N—H bonds is retained. There appear to be two possible ways in which chain growth can satisfy these conditions, as indicated schematically in Figures 12*a* and 12*b*. These alternatives would lead to polymers of one of two types as shown on Figure 13. We hope to present later spectroscopic evidence distinguishing between these two possibilities, which seems to indicate that structure I is favored in solid-state polymerization. At present, we should only like to note that structure I, resulting from a head-to-head polymerization, is a type of polymer which cannot be made in the liquid state. Structure II is a derivative of syndiotactic polystyrene which should, in principle, be obtainable in liquid phase polymerization but has not been reported to date. If the polymers are represented by structure I, the individual chains should be optically active and although one would

expect equal numbers of *d* and *l* chains to be formed, it might be possible to resolve the mixture by adsorption chromatography.[19] If head-to-head polymerizations can occur in the crystalline state and if a monomer susceptible to this type of chain growth forms crystals in a space group which exhibits crystal enantiomorphy, it would be possible to separate mechanically *d* and *l* crystals and to polymerize each to an optically active product without the use, at any state of the preparation, of an optically active reagent.

The interpretation of the results obtained with AAS is more uncertain. The fact that the front of the polymer phase may advance a distance which is many times as great as the thickness of the crystal platelet while the residual monomer, in the center of the platelet, remains apparently unaltered, suggests that polymerization is impossible in the direction perpendicular to the large face of the crystal. This, as we have seen, is the direction perpendicular to the sheets containing the vinyl groups. Although the phase boundary within the birefringent region of a partially polymerized single crystal (see Fig. 7) suggests that the polymer first forms in an oriented state, the study of this state is rendered difficult by the fact that the polymerization is too slow for investigation below the glass transition temperature of the polymer. Thus, the oriented poly-AAS represented merely a short-lived intermediate state under the experimental conditions employed. It may be noted, however, that a polymerization of AAS directed by the geometry of the monomer crystal lattice would differ in one important respect from the analogous process with BAS: whereas the polymer molecules or poly-BAS would be expected to be hydrogen-bonded intramolecularly, the disposition of the monomer molecules of AAS is such that the polymer would have to form as intermolecularly hydrogen-bonded sheets. This difference is apparent from a comparison of Figures 5 and 6.

Finally we should comment on the unusual fact that the polymerization of both AAS and BAS led to a volume expansion. Such an expansion might be expected whenever a crystalline monomer carries very bulky substituents, since the disorientation of the efficient packing characterizing the monomer crystal lattice will more than compensate for the contraction due to the conversion of the vinyl groups into a continuous carbon chain.

EXPERIMENTAL

Monomer Preparations

The monomers were prepared by acylation of *p*-aminostyrene obtained from *p*-aminophenethyl alcohol. The dihydration of the alcohol was carried out by a modification of the method described by Sabetay.[20] The AAS crystals were recrystallized repeatedly from ethyl acetate, the BAS from triethyl orthoformate until a colorless product of constant melting point T_m was obtained. Since the crystals polymerized rapidly below T_m, the oil bath used for melting point determinations had to be pre-

heated to a temperature 3–4°C. below the presumed value of T_m before inserting the crystal sample. In this manner the determination could be completed in less than two minutes and consistent results could be obtained (T_m = 146°C. for AAS, T_m = 176–177°C. for BAS).

X-Ray Diffraction

Precession pictures and Weissenberg photographs were taken to determine the lattice constants and the space group of the monomer using CuKα radiation.

Kinetic Studies

The polymerization reaction was followed by infrared spectroscopy using either polycrystalline samples in a KBr pellet or single crystals with a surface area of 8–10 mm.^{2} and a thickness of about 2μ. The KBr pellet was mounted in a specially designed heating unit which could be inserted into a Perkin-Elmer Model 21 infrared spectrophotometer. The heating unit consisted of an electrically heated brass block insulated with Teflon and the control system allowed maintenance of constant temperature within 0.1°C. For temperature calibration, KBr pellets containing acetanilide (m.p. 114°C.) benzoin (m.p. 137°C.) and benzanilide (m.p. 161°C.) were used, the temperature at which the opacity of the pellet disappeared being observed. The single crystals were placed on a KBr pellet with a shallow well and were covered with a second pellet. Aluminum foil was used to block the radiation outside the area occupied by the test crystal.

Monomer conversion was followed by changes in the intensity of the band at 996 cm.$^{-1}$ for AAS and 992 cm.$^{-1}$ for BAS (C—H out-of-plane deformation of the vinyl group[21]). Monomer concentration was assumed to be proportional to the optical density at the peak of the absorption band. The effect of exposure to ionizing radiation was studied in microcrystalline AAS samples incorporated into KBr pellets, which were irradiated under vacuum at −78°C. with gamma rays from a Co^{60} source with a dose of 0.5 or 1.0 Mrad, before warming the specimen to the polymerization temperature.

Infrared Dichroism

An infrared polarizer consisting of six parallel silver chloride sheets set at an angle of 26°53′ to the direction of the light beam was used for a study of the infrared dichroism of single BAS crystals. An adjustable attenuator was used in the reference beam.

Microscopy

A Zatopan Model microscope manufactured by Reichert (Vienna) was used in combination with a specially designed thermostatted heating stage. Photographs of the appearance of single crystals in polarized light were taken with the analyzer set at an angle of 75° to the polarizer, so as to reveal the

Becke lines at the phase boundaries of the isotropic portions of the specimen.

Electron Microscopy

A Siemens 100 k.v. electron microscope was used for photographing replicas of the surface of BAS crystals at various stages of the spontaneous polymerization. The crystals were shadowed with platinum at an angle of 30° and coated with a carbon film. Monomer and polymer were dissolved by treatment with dimethylformamide.

Polymer Characterization

The chain length of polymers was characterized by the measurement of solution viscosity in pyridine at 25°C., with an Ubbelohde dilution viscometer. The glass transition temperatures of AAS and BAS were obtained as the break in the volume–temperature plot of the bulk polymer, a dilatometer similar to that described by Bekkedahl and Wood[22] being used. More consistent data were obtained with rising temperatures.

We wish to thank Dr. Fraser P. Price and Mr. W. J. Barnes of the General Electric Company for the electron microscopy investigation. We also wish to acknowledge helpful discussions with Professor B. Post of the Physics Department concerning the crystal structures of the monomers. Finally we should like to express our gratitude to Dr. H. Ringsdorf, who drew our attention to reference 12 and was in this way largely responsible for the initiation of this research.

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Synopsis

Spontaneous thermally initiated polymerization was observed in crystalline *p*-acetamidostyrene (AAS) up to 50°C. below its melting point and in *p*-benzamidostyrene (BAS) up to 70°C. below its melting point. The kinetics of the process were followed by infrared spectroscopy. The polymerization of AAS crystals was 5–6 times slower than that in liquid AAS-acetanilide mixtures containing 47 mole-% AAS; the activation energies corresponding to initial rates were 18 and 21 kcal./mole, respectively. The initial rates of BAS solid state polymerization had an activation energy of 42 kcal./mole. The initial stages of the reactions proceeded at constant rate with no induction period; at higher conversion the rate accelerated with AAS crystals, slowed down with AAS solutions and decreased abruptly to a lower constant rate with BAS crystals. The initial polymerization rate of crystalline AAS was less than doubled by preirradiation with a dose of 0.5 Mrad. Solution viscosity measurements showed that the chain length of the polymers is independent of conversion but tends to increase with the temperature at which the crystalline monomers were polymerized. Observations of polymerizing AAS crystals under the polarizing microscope suggested that the polymer is first formed in an ordered form and becomes isotropic only in a subsequent relaxation process. With BAS single crystals it was demonstrated that polymerization below 120°C., the glass transition temperature of the polymer, leads to a highly ordered product in which the infrared dichroism of the bands due to N—H and C=O stretching vibrations is the same as in the parent monomer. The birefringence of the monomer crystal in visible light is also largely preserved during polymerization below 120°C. Electron microscopic observation of the surface of BAS crystals in various stages of the polymerization process reveal deep-seated changes at very low degrees of conversion, the oriented structure of the polymer formed in the later stages and a characteristic difference in the appearance of specimens heated below and above the glass transition temperature of the polymer. It is shown that chain propagation parallel to the *b* axis of BAS is possible without introducing large stresses into the polymer chain. The polymer is believed to have either a *threo* head-to-head, tail-to-tail or a syndiotactic structure with all hydrogen bonding intramolecular in either case.

Résumé

On a observé une polymérisation spontanée, due à une initiation thermique, du *p*-acétamidostyrène (AAS) à l'état cristallin jusqu'a une température inférieure de 50°C à son point du fusion ainsi que de *p*-benzamidostyrène (BAS) jusqu'a une température inférieure de 70°C à son point de fusion. La cinétique de ces réactions a été suivie par spectroscopie infrarouge. La polymérisation de cristaux d'AAS est 5 à 6 fois plus lente que celle de mélanges liquides AAS-acétanilidine contenant 47 mole % d'AAS. Les énergies d'activation se rapportant aux vitesses initiales sont de 18 et 21 kcal/mole respectivement. La vitesse initiale de polymérisation du BAS présente une énergie d'activation de 42 kcal/mole. Le stade initial des réactions se déroule à vitesse constante sans période d'induction. À pourcentages de conversion plus élevés, la vitesse accélère dans le cas de cristaux d'AAS, ralentit dans le cas de solutions d'AAS et décroit brusquement justqu'à une vitesse constante plus faible dans le cas de cristaux de BAS. La vitesse de polymérisation initiale de l'AAS à l'état cristallin n'est pas tout à fait doublée sin on effectue une préirradiation avec une dose de 0.5 mégarads. Des mesures viscosimétriques en solution montrent que la longueur de chaîne des polymères est indépendante du degré de conversion mais a tendance à augmenter avec la température à laquelle le monomère cristallin a été polymérisé. L'observation au microscope polarisant de cristaux d'AAS en train de polymériser, suggère que le polymère commence par se former d'une façon ordonnée, puis dans la suite devient isotrope au cours di'un processus

de rélaxation. Avec de simples cristaux de BAS, on montre que la polymérisation effectuée en-dessous de 120°C (la température de transition vitreuse du polymère) conduit à un produit fortement ordonné dans lequel le dichroïsme infra-rouge des bandes dues aux vibrations d'étirement (stretching) des groupes NH et CO est identique à celui du monomère correspondant. La biréfringence du monomère cristallin à la lumière visible est aussi largement conservée au cours de la polymérisation effectuée en-dessous de 120°C. L'observation au microscope électronique de la surface de cristaux de BAS à différents stades du processus de polymérisation révèle des modifications localisées en profondeur aux faibles degrés de conversion, une structure orientée du polymère formé aux stades ultérieurs et une différence caractéristique entre l'aspect des échantillons chauffés à des températures inférieures et supérieures à la température de transition vitreuse du polymère. On montre que la propagation dans une direction parallèle à l'axe *b* du BAS est possible sans introduire des tensions importantes dans la chaîne polymérique. On croit que le polymère possède soit une structure *thréo*-tête-à-tête, soit une structure syndiotactique avec des liens hydrogènes intramoléculaires dans chacun des cas.

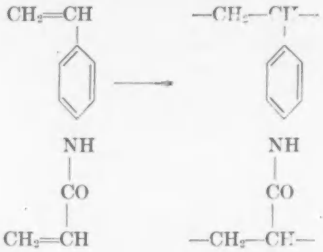
Zusammenfassung

In kristallinem *p*-Acetamidostyrol (AAS) wurde bis zu 50°C unterhalb des Schmelzpunktes, in *p*-Benzamidostyrol (BAS) bis zu 70° unterhalb des Schmelzpunktes spontane thermisch gestartete Polymerization beobachtet. Die Kinetik der Reaktion wurde IR-spektroskopisch untersucht. Die Polymerisation von AAS-Kristallen verlief 5–6 mal langsamer als diejenige in flüssigen AAS-Acetanilid-Gemischen mit einem Gehalt von 47 Mol-% AAS. Die der Anfangsgeschwindigkeit entsprechende Aktivierungsenergie war 18 bzw. 21 kcal/Mol. Die Anfangsgeschwindigkeit der BAS-Polymerisation entsprach einer Aktivierungsenergie von 42 kcal/Mol. Die Anfangsperiode der Reaktion verlief mit konstanter Geschwindigkeit und ohne Induktionsperiode. Bei höheren Umsätzen nahm die Geschwindigkeit im Falle der AAS-Kristalle zu, bei AAS-Lösungen ab und sank bei BAS-Kristallen plötzlich auf eine niedrigere, konstante Geschwindigkeit. Die anfängliche Polymerisationsgeschwindigkeit von kristallinem AAS wurde durch Vorbestrahlung mit einer Dosis von 0,5 Megarad auf etwas weniger als das Doppelte erhöht. Wie Lösungsviskositätsmessungen zeigen, ist die Kettenlänge der Polymeren vom Umsatz abhängig, nimmt aber mit der Temperatur, bei der das kristalline Monomere polymerisiert wird, zu. Die Beobachtung polymerisierender AAS-Kristalle unter dem Polarisationsmikroskop weist darauf hin, dass das Polymere zuerst in geordnetem Zustand gebildet und erst in einem darauffolgenden Relaxationsprozess isotrop wird. Die Polymerisation von BAS-Einkristallen unterhalb von 120°C, dem Glasumwandlungspunkt des Polymeren, ergibt ein weitgehend geordnetes Produkt mit demselben IR-Dichroismus der den N—H- und C=O-Valenzeschwingungen entsprechenden Banden (wie das ursprüngliche Monomere. Die Doppelbrechung des Monomerkristalls im sichtbaren Licht bleibt bei der Polymerisation unterhalb 120°C ebenfalls weitgehend erhalten. Die elektronenmikroskopische Beobachtung der Oberfläche der BAS-Kristalle in verschiedenen Stadien der Polymerisation zeigt tiefgreifende Veränderungen bei sehr niedrigen Umsätzen, die Orientierung des in den späteren Stadien gebildeten Polymeren charakteristischen Unterschied im Aussehen der Proben bei Temperaturen unterhalb und oberhalb des Glasumwandlungspunktes des Polymeren. Das Kettenwachstum längs der *b*-Achse von BAS ist ohne das Auftreten grosser Spannungen in der Polymerkette möglich. Man nimmt an, dass das Polymere entweder eine *threo*-Kopf-Kopf-, -Schwanz-Schwanz- oder eine syndiotaktische Struktur besitzt und dass in jedem Falle alle Wasserstoffbrückenbindungen intramolekular sind.

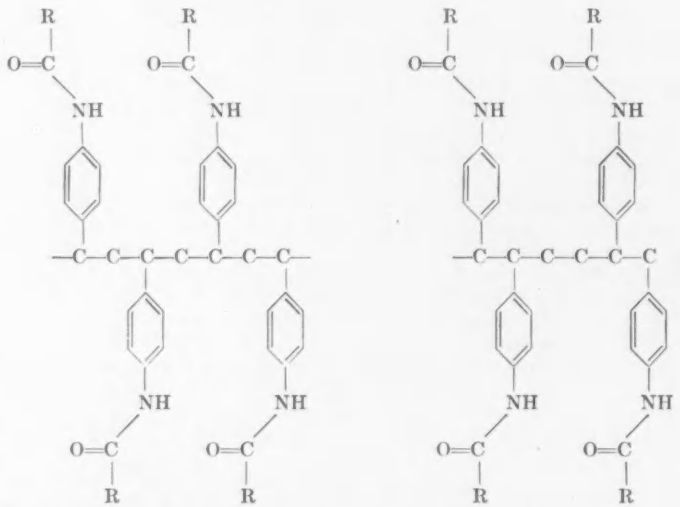
Discussion

H. Ringsdorf (*Universität Marburg, Germany*): You could show that in the crystals of acetamidostyrene and benzamidostyrene the reactive vinyl groups lie in sheets. Do

you think that due to this fact it might be possible to prepare "ladder" type polymers by polymerizing *p*-acrylamidostyrene in the solid state?



H. Morawetz: We have tried to polymerize both *N*-acrylamidostyrene and *N*-methylacrylamidostyrene in the crystalline state and both reactions take place easily by a thermal initiation mechanism. However, it must be taken into account that if polymerization is to take place yielding oriented chains without introducing excessive stresses, *two sheets* of hydrogen-bonded monomers have to participate in the formation of one chain. The chain may then have one of two structures which appear in projection as



It would then appear that if the R residues have a polymerizable double bond, these bonds would be too far from each other for the formation of a ladder polymer.

E. Selegny (*Faculté des Sciences, Nantes, France*): Avez-vous essayé la polymérisation en phase solide du *p*-aminostyrène (ou de ses sels?) Nous avons en effet remarqué au cours d'un travail antérieur (*Bull. Soc. Chim.*, pp. 1280, 1281 (1959)) que cette réaction était possible.

H. Morawetz: We have been unable to polymerize in the crystalline state either *p*-aminostyrene or its chloride. This is in agreement with your results, since you state in the paper you cite that *p*-dimethylaminostyrene tends to polymerize in the solid state while *p*-aminostyrene crystals are stable on storage.

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Cationic Polymerization of Trioxane in Solid Phase

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I. INTRODUCTION

Recently, studies of the solid-state polymerization induced by gamma-ray irradiation have been reported.[1,2] In some cases the rate of polymerization in the solid state was found to be higher than that in the liquid state. Moreover, it has been recognized that the polymer was in an oriented crystalline state in several cyclic compounds.[2] From the fact that these cyclic compounds could be polymerized only by ionic catalyst, it might be assumed that polymerization in the solid state took place by an ionic mechanism.

The cationic-catalyzed polymerization of trioxane in the solid state was reported previously.[3] The polymerization of solid monomer induced by ionic catalyst represented some peculiar behavior compared to the ionic polymerization in liquid state. It is possible that the arrangement of molecules in the monomer crystal influence the polymerization kinetics and also the orientation of polymer chain. Studies on the polymerization in solid phase might provide some information concerning the diffusion of counterion.

For this reason, trioxane was used here as monomer, and the solid-state polymerization of a suspension of trioxane crystals in *n*-hexane containing $BF_3 \cdot OEt_2$ was studied.

II. EXPERIMENTAL

Materials

Trioxane was purified twice by recrystallization from the CH_2Cl_2 solution. Large crystals of trioxane (L), $\sim$ 3 mm. diameter $\times$ 30 mm. were obtained by slow cooling of the CH_2Cl_2 solution and dried over KOH in a desiccator. Small crystals (S), $\sim$1 mm. diameter $\times$ 10 mm. were prepared by rapid cooling. After drying for a week, H_2O content was about 0.008%.

The catalysts ($BF_3 \cdot OEt_2$, $SnCl_4$, and $TiCl_4$ with CCl_3COOH) and the dispersing medium (*n*-hexane) were purified in the usual way.

Procedure

Polymerization in the solid state was carried out on a suspension of trioxane in *n*-hexane containing $BF_3 \cdot OEt_2$ as catalyst. As the solid monomer is dipped in a catalyst solution, the crystalline solid monomer becomes turbid by instant polymerization. The polyoxymethylene obtained was separated by filtration through a glass filter and washed repeatedly with MeOH–NH_4OH and MeOH. The polymer was then dried in vacuum at room temperature.

The determination of viscosity number (η_{sp}/c) of the polymer was carried out in a *p*-chlorophenol solution containing 2% α-pinene at a polymer concentration of 0.5% at 60°C. in nitrogen atmosphere.

The x-ray diffraction diagrams of the polymer were taken with a Shimazu GX-II type diffractometer using 35 kvp, 15 ma. Ni-filtered CuKα rays. The exposure time was 30 min. at a distance of ca. 25 mm.

III. RESULTS

Rate of Polymerization

Figure 1 shows the results on the rate of polymerization at 30°C. with various kinds of catalysts. The rates of polymerization decrease in the following order: $BF_3 \cdot OEt_2 > SnCl_4 > TiCl_4$. This order may have some

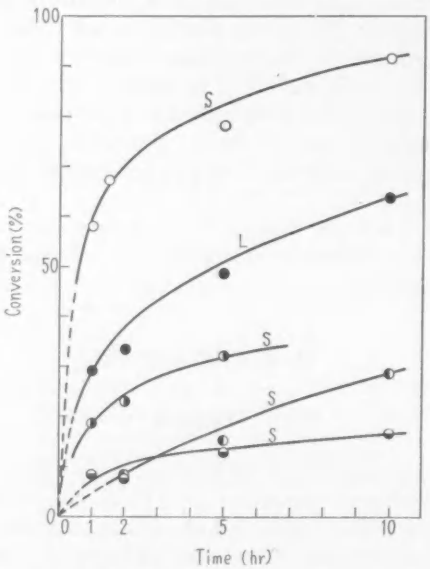


Fig. 1. Cationic polymerization of trioxane in solid state with various catalysts at 30°C.: (○, ●) $BF_3 \cdot OEt_2$; (◑) $SnCl_4$–TCA (2:1); (◐) $SnCl_4$; (⊖) $TiCl_4$–TCA (2:1). [M] = 0.74 mole/l. in *n*-hexane, [C] = 45.0 mmole/l.

meaning as discussed in the following section. The saturation phenomenon of polymer yield observed in the radiation-induced polymerization[4] was not observed here. Moreover, it was found that trioxane polymerizes more easily in small crystals than in large ones, while opposite results were obtained in the case of radiation polymerization.[4] From these results, it may be concluded that polymerization proceeds from the surface of solid monomer.

The effect of catalyst concentration is shown in Figure 2.

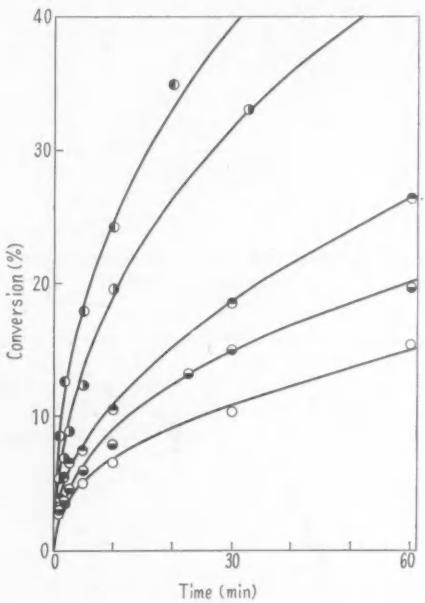


Fig. 2. Polymerization of trioxane in solid state at various concentrations of $BF_3 \cdot OEt_2$ catalyst at 30°C.: (◐) 45.0 mmole/l.; (◑) 22.5 mmole/l.; (◓) 11.25 mmole/l.; (◒) 5.63 mmole/l.; (○) 4.50 mmole/l. [M] = 0.74 mole/l. in *n*-hexane, small crystals.

The relation between the initial rate and catalyst concentration is plotted in Figure 3. In the range of 4.5–45 mmole/l., the initial rate is found to be proportional to catalyst concentration.

Time–conversion curves at various monomer concentrations are shown in Figure 4. The conversion is independent of the initial monomer concentration, and thus the rate of polymerization is proportional to the initial monomer concentration. The initial rate may be described by eq. (1):

$$R_{p0} \doteq k[C]_0[M]_0 \tag{1}$$

where the initial monomer concentration $[M]_0$ is 0.37–1.10 mole/l. and the initial catalyst concentration $[C]_0$ is 4.5–45.0 mmole/l.

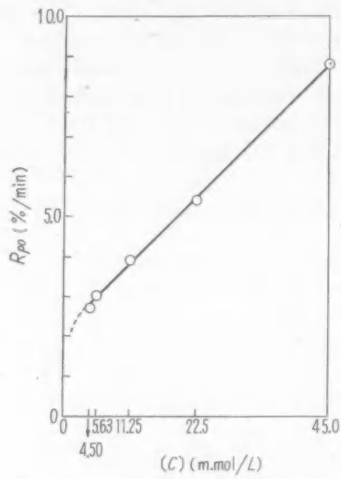


Fig. 3. Dependence of the initial rate on catalyst concentration. Reaction conditions are the same as in Fig. 2.

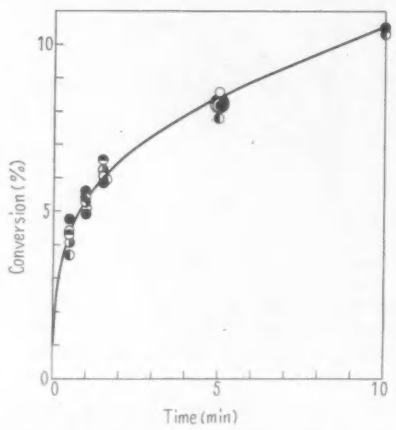


Fig. 4. Dependence of the initial rate on monomer concentration (small crystals) in *n*-hexane at 30°C.: (○) 1.10 mole/l.; (●) 0.74 mole/l.; (◑) 0.555 mole/l.; (◐) 0.44 mole/l.; (◓) 0.37 mole/l. $[BF_3 \cdot OEt_2] = 11.25$ mmole/l.

Effect of Polymerization Temperature

It has been established in the case of radiation-induced polymerization that the rate of polymerization changed at the phase transition of the solid monomer. In this connection, the dependence of the initial rate on the polymerization temperature was studied; the results are shown in Figure 5.

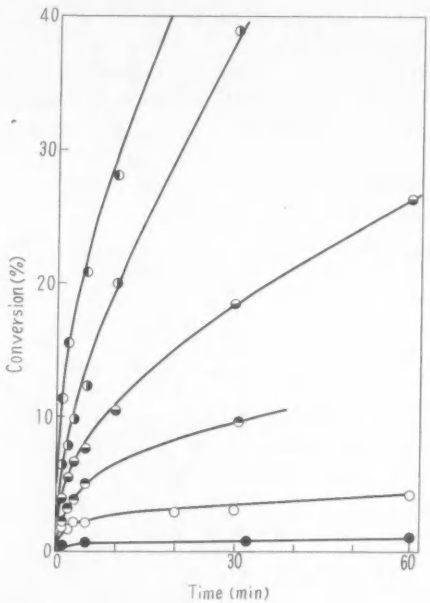


Fig. 5. Dependence of the initial rate on the polymerization temperature: (◐) 50°C.; (◑) 40°C.; (◒) 30°C.; (◓) 20°C.; (○) 10°C.; (●) −20°C. [M] = 0.74 mole/l. in *n*-hexane, small crystals. $[BF_3\text{-}OEt_2]$ = 11.25 mmole/l.

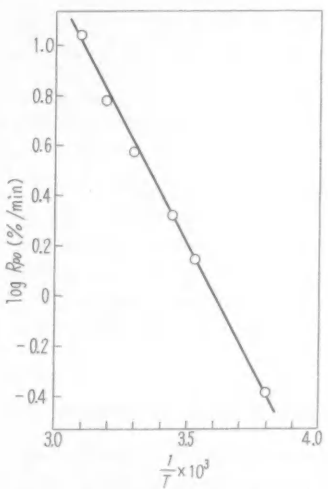


Fig. 6. Arrhenius plots between the initial polymerization rate and temperature (ΔE = 8.6 kcal./mole).

The rate of reaction is not reproducible enough at 30°C., which seems to correspond to a phase transition.

From the results mentioned above the activation energy in the initial rate of polymerization is estimated to be 8.6 kcal./mole in the range from −20 to 50°C., as shown in Figure 6.

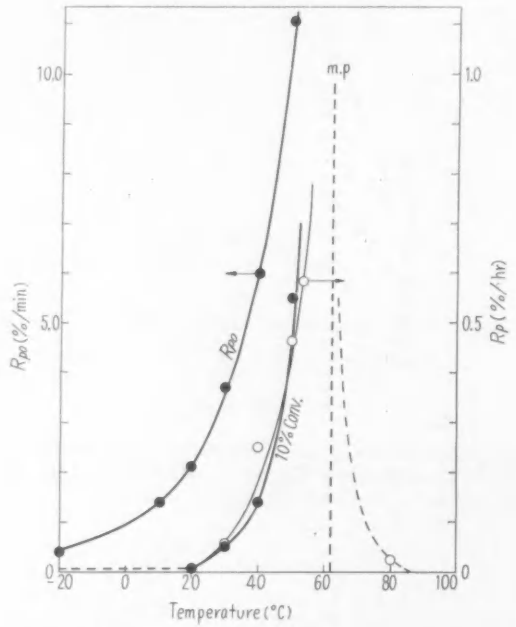


Fig. 7. The relation between the rate and temperature of polymerization: (●) cationic polymerization (reaction conditions are the same as in Fig. 5); (○) radiation-induced polymerization,[5] 1.1×10^4 r/hr.

On comparing the rate of polymerization induced by cationic catalyst with that of radiation-induced polymerization (especially at 10% conversion) (Fig. 7), an extremely low rate of reaction is observed in the solid-state polymerization at low temperature below ca. 20–30°C. The mobility of monomer molecules in crystalline solid seems to be strongly restricted at lower temperatures.

Solution Viscosity of Polymer Obtained

The viscosity number of the polymer obtained by cationic polymerization in the solid phase decreased remarkably as the yield of polymerization increased (Fig. 8). The dependence of the viscosity number on the catalyst concentration was investigated (Fig. 8), but no differences were found.

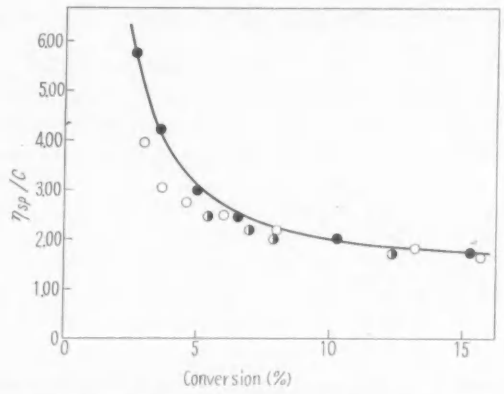


Fig. 8. Dependence of η_{sp}/C on the concentration of catalyst. [C]: (●) 4.5 mmole/l.; (○) 5.63 mmole/l.; (◑) 22.5 mmole/l. Polymerization conditions are the same as in Fig. 2.

The viscosity number, however, increased unexpectedly with increasing the polymerization temperature (Fig. 9). From these results the number of the polymer chain is deduced. Figure 10 shows that the number of polymer chain increased as the conversion of polymer increased and decreased when the temperature of polymerization was raised.

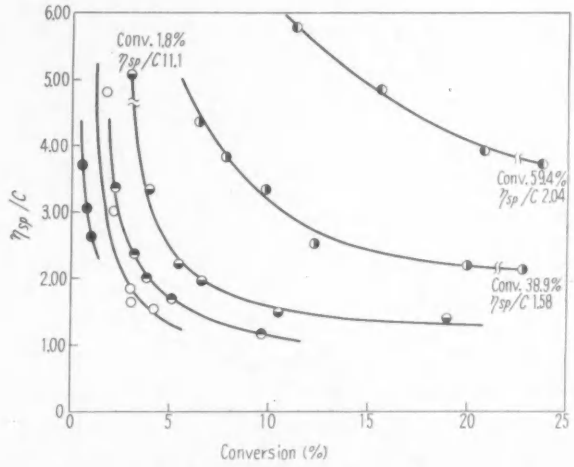


Fig. 9. Effect of polymerization temperature on the molecular weight of polymer: (◐) 50°C.; (◑) 40°C.; (◒) 30°C.; (◓) 20°C.; (○) 10°C.; (●) −20°C. Polymerization conditions are the same as in Fig. 5.

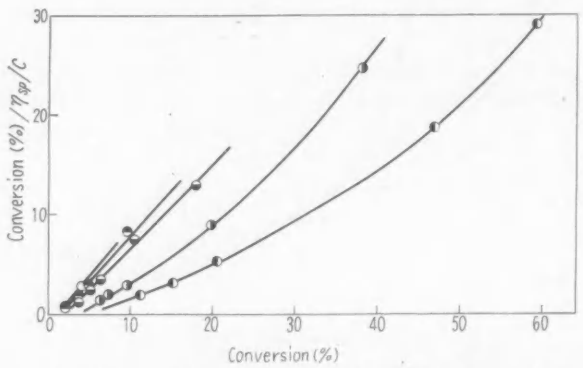


Fig. 10. Change of the number of polymer chain in solid-phase polymerization at various polymerization temperatures: (◐) 50°C., (◑) 40°C.; (◒) 30°C.; (◓) 20°C.; (○) 10°C.

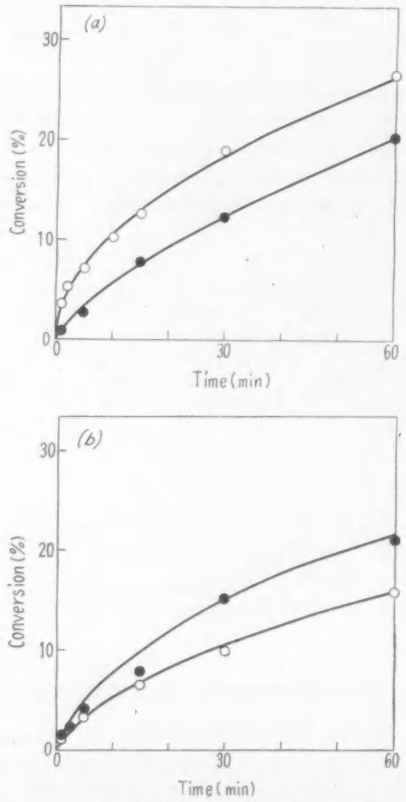


Fig. 11. The rates of polymerization in (●) liquid and (○) solid at 30°C. with various catalysts: (*a*) BF_3-OEt_2; (*b*) $SnCl_4$–CCl_3COOH (2:1). [M] = 0.444 mole/l. in *n*-hexane, small crystals; [C] = 11.25 mmole/l.

Effect of Monomer Phase

As shown in Figure 2, the initial rate of polymerization is unexpectedly rapid in spite of the fact that monomer molecules cannot move freely in the crystalline state as they can in the liquid phase. A comparison is made of the rates and the degrees of polymerization in the solid and in the liquid states (Figs. 11 and 12).

In the solid phase, the rates of polymerization induced by $BF_3 \cdot OEt_2$ catalyst are found to be higher than those of $SnCl_4$. In the solution system, on the other hand, this relation is just in the reverse.

The molecular weight of polymers obtained in the solid phase is found to be extremely high in comparison with those derived in the solution system.

X-Ray Diffraction Diagram

The structure of polymers obtained was examined by x-ray diffraction analysis. X-ray diffraction diagrams of polyoxymethylene obtained in solid phase by $BF_3 \cdot OEt_2$ catalysis at high temperature show that the polymer molecules are highly oriented (Fig. 13*b*). Lowering polymerization temperature or using $SnCl_4$ catalyst decreases the degree of orientation (Fig. 13*a*). The twin structure of polyoxymethylene obtained in the

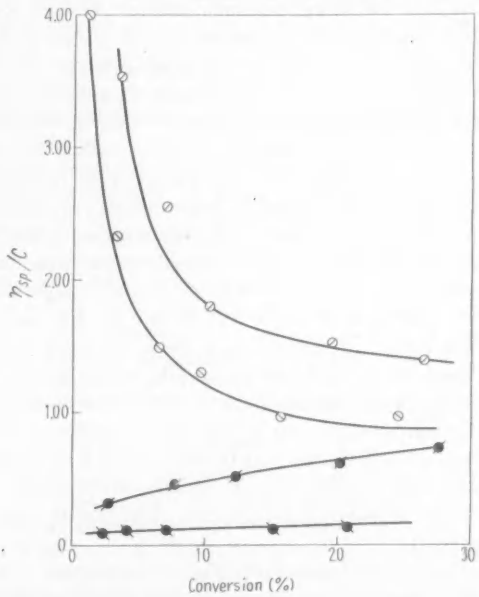
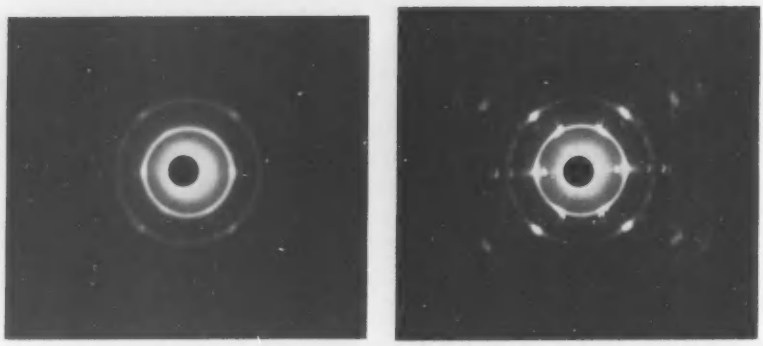


Fig. 12. Comparison between molecular weight in polymerization in solid and liquid phases: (⊘) solid state, $BF_3 \cdot OEt_2$ catalyst; (⊘) solid state, $SnCl_4$ catalyst; (●) liquid state, $BF_3 \cdot OEt_2$ catalyst; (●) liquid state, $SnCl_4$ catalyst.

radiation-induced solid-state polymerization[2] is also observed in polymers obtained by cationic catalyst.



(*a*) (*b*)

Fig. 13. X-ray diffraction diagrams of polyoxymethylene polymerized in solid state by $BF_3 \cdot OEt_2$ catalyst at various polymerization temperatures: (*a*) 5°C., (*b*) 55°C. In the case of (*b*), both the spots from polymer and those of monomer are shown.

IV. DISCUSSION

Solid-phase polymerization of trioxane crystals directly induced by the gaseous or liquid Friedel-Crafts catalysts results in low molecular weight polyoxymethylene having a high degree of orientation in high yield.[3]

Monomer crystal was added to *n*-hexane homogeneously containing catalyst in order to determine the exact degree of catalyst concentration and also to avoid the degradation of polymer by excess catalyst. In this case, an extremely high molecular weight polymer was obtained, as shown in Figures 8 and 9, and the rate of polymerization is also relatively high in comparison with that in the usual liquid-state polymerization as represented in Figure 11. The solid-state reaction might have a slower rate than the liquid-state reaction because of lower mobility of reactant molecules in the solid phase. This is found here not to be in the case for the polymerization of trioxane in solid state. In the solution polymerization the rate of polymerization is larger with $SnCl_4$ than with $BF_3 \cdot OEt_2$, but in the solid-state polymerization the reverse relation is clearly shown in Figures 1 and 11. The degree of orientation is low in the case of $SnCl_4$. The diffusion of large counterions into the inner part of the crystal may be somewhat difficult in the case of $SnCl_4$ catalyst, and the rate of diffusion of counteranion may have a certain influence upon the rate of solid-state polymerization of trioxane crystal induced by cationic catalyst.

In the radiation-induced polymerization, a larger rate of polymerization was obtained in the case of larger monomer crystals formed by slow cooling, but in the catalytically induced solid-state polymerization the rate of polymerization is found to be larger in the case of small crystals as shown in

Figure 1, because of their larger specific surface area. The polymerization reaction proceeds from the surface of monomer crystal as seen in the external appearance.

An increase of the temperature of polymerization reduces the decrease of molecular weight during polymerization and increases the orientation. The reorientation of polymer molecules during polymerization and the polymerization reaction becomes easier at high temperature. Below ca. 20–30°C., the movement of monomer molecules may become more inhibited, and then the polymerization behavior changes at the transition temperature of the monomer in the solid state at ca. 20–30°C.

The activation energy of polymerization is estimated here to be 8.6 kcal./mole, instead of 19 kcal./mole for polymerization in a $(CH_2Cl)_2$ solution.[6] The preorientation of monomer molecules in the crystalline state may facilitate energetically the polymerization reaction in the solid state.

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6. Okamura, S., T. Higashimura, and M. Tomikawa, paper presented at meeting of the High Polymer Chemistry, Osaka, Japan, November, 1962.

Synopsis

Trioxane can be polymerized into a high molecular weight polymer in high yield by solid-state polymerization in *n*-hexane by using $BF_3 \cdot OEt_2$ as catalyst. Especially at the early stage of polymerization, both the rate and the degree of polymerization were extremely high. During polymerization, a decrease of molecular weight was observed; this was considered to constitute formation of low molecular weight polymer, not as the degradation of the polymer formed. The rate of polymerization increased as the temperature of polymerization increased. The apparent activation energy was estimated to be 8.6 kcal./mole; this is smaller than that of solution polymerization. The degree of orientation of polymer molecules determined by x-ray diffraction and the molecular weight were found to be higher in the case of polymerization at high temperature than that at low temperature. From the dependence of polymerizing temperature there seemed to be in a transition temperature at about 20–30°C. for the movement of monomer molecules in solid crystals. The polymerization reaction was considered to proceed from the surface into the inner part of monomer crystal, as the monomer crystals having the larger surface area had a larger rate of polymerization.

Résumé

On reconnait que le trioxane polymérise pour donner un polymère de haut poids moléculaire avec un rendement élevé par polymérisation à l'état solide dans l'hexane-*n* avec BF_3-OEt_2 comme catalyseurs. C'est spécialement aux derniers stades de la polymérisation que la vitesse et la degré de polymérisation sont extrèmement élevés. Durant la polymérisation on observe une diminution du poids moléculaire et on considère que cela est dû à la formation du polymère de faible poids moléculaire et non à la dégradation du polymère formé. La vitesse de polymérisation augmente lorsqu'on élève la température de polymérisation et on évalue l'énergie d'activation apparente à 8.6 kcal/mole; elle est plus petite que celle de la polymérisation en solution. On trouve que le degré

d'orientation des molécules de polymère déterminé par rayons-X et le poids moléculaire sont plus élevés dans le cas de la polymérisation à haute température que dans le cas de la polymérisation à basse température. A partir de la dépendance de la température de polymérisation il semble y avoir une température de transition d'environ 20–30°C pour le mouvement des molécules de monomère dans les cristaux solides. On considère que la réaction de polymérisation procède à partir de la surface dans la partie interne du cristal de monomère en tenant compte du fait que le cristal du monomère à grande surface de contact a une grande vitesse de polymérisation.

Zusammenfassung

Es wurde gezeigt, dass Trioxan in hoher Ausbeute zu einem hochmolekularen Polymeren durch Polymerisation in fester Phase in *n*-Hexan mit $BF_4 \cdot OEt_2$ als Katalysator polymerisieren kann. Besonders im Anfangsstadium der Polymerisation waren Geschwindigkeit und Polymerisationsgrad extrem hoch. Während der Polymerisation wurde eine Abnahme des Molekulargewichtes beobachtet, die auf eine Bildung niedermolekularer Polymerer und nicht auf Abbau des gebildeten Polymeren zurückgeführt wurde. Die Polymerisationsgeschwindigkeit nahm mit steigender Polymerisationstemperatur zu und die scheinbare Aktivierungsenergie wurde zu 8,6 kcal/Mol, kleiner als die der Lösungspolymerisation, bestimmt. Der durch Röntgenbeugung bestimmte Orientierungsgrad der Polymermoleküle sowie das Molekulargewicht lagen im Falle der Hochtemperaturpolymerisation höher als bei Tieftemperaturpolymerisation. Aus der Abhängigkeit von der Polymerisationstemperatur scheint sich für die Bewegung der Monomermoleküle im festen Kristall eine Umwandlungstemperatur von etwa 20–30°C zu ergeben. Auf Grund der Tatsache, dass eine Monomerkristall mit grosser Oberfläche eine grosse Polymerisationsgeschwindigkeit besitzt, wurde angenommen, dass die Polymerisationsreaktion von der Oberfläche ins Innere des Monomerkristalles fortschreitet.

Discussion

H. Sack (*Houillères du Nord, Paris, France*): (*1*) Si on disperse du trioxane préirradié aux rayons gamma dans un solvant lui même saturé de trioxane, à la température de polymérisation, on constate une modification importante de la cinétique par rapport à une polymérisation analogue effectuée sans mileu de dispersion: les rendements diminuent et les viscosités réduites deviennent faibles. Ces phénomènes se vérifient même dans le cas de cristaux de taille relativement grande. Il y a donc incontestablement diffusion rapide du solvant, même saturé, à l'intérieur des cristaux. Il est probable que dans les expériences décrites par la Professeur Okamura et coll., la diffusion du solvant et du catalyseur à l'intérieur des cristaux contribue considérablement aux conditions cinétiques.

(*2*) On peut effectuer des polymérisations cationiques du trioxane à l'état solide, le catalyseur à l'intérieur du cristal lui même. Il suffit d'injecter dans du trioxane fondu à une température légèrement supérieure au point de fusion, quelques dixaines de ppm d'un mauvais catalyseur (par exemple, acide sulfurique dissous dans l'éther éthylique ou acide toluène sulfonique, etc;). En effectuant alors une cristallisation lente par abaissement de la température de quelques degrés, on constate que la cristallisation s'accompagne d'une abondante formation de polyoxyméthylène fibreux.

S. Okamura: (*1*) It may be very interesting to try solid-state polymerization by using other kinds of acid catalysts like sulphuric acid. However, unless the catalyst used acts as a strong catalyst for trioxide, the surface of trioxane may resolve into the suspending medium gradually.

(*2*) Trioxane can be polymerized also by post-reaction in the solid state. Irradiated trioxane crystals suspended in *n*-hexane and heated at 50°C. may lead to a polymerization in the solid state, but at this time I have no experimental data on such a procedure.

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Structure of Polymers Formed by Radiation-Induced Solid-Phase Polymerization of Cyclic Monomers

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I. INTRODUCTION

It has been known since the first report on the radiation-induced cationic polymerization of isobutene[1] that radiation-initiated reaction could cover not only the radical polymerization but also ionic polymerization. Thus the kinds of monomers which can be polymerized by irradiation included aldehydes[2] and nitriles.[3] The radiation-induced ionic polymerization was found to proceed easily at low temperature or in the solid state. For example, β-propiolactone,[4] 3,3-bischloromethylcycloxabutane,[5] trioxane,[6] and tetraoxane[7] were all very easily polymerizable in the solid state by gamma-irradiation. On solid-state polymerizations of these four-, six-, and eight-membered cyclic monomers, the external appearance of the crystals remains the same in the whole range of polymerization from monomer to its polymer. In the present paper, experimental results are described, and a preliminary discussion is given of the structure of polymer obtained by solid-state polymerization of these cyclic monomers.

II. EXPERIMENTAL

Monomers

β-Propiolactone was dehydrated with dry Na_2SO_4 and distilled twice at 10 mm. Hg pressure. 3,3-Bischloromethylcycloxabutane was distilled and recrystallized by slow cooling. Trioxane was recrystallized by cooling from the methylenechloride solution or by sublimation and condensation. Tetraoxane was produced by the thermal decomposition of acetylated paraformaldehyde and recrystallized by cooling from carbon disulfide solution.

Polymerization

γ rays from a Co^{60} source were used for irradiation. After irradiation, the monomer remaining in the crystal was removed by methanol extraction in the cases of β-propiolactone, 3,3-bischloromethylcycloxabutane,

and trioxane, and by acetone extraction in the case of tetraoxane, both before drying in vacuum at ca. 50°C.

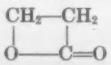
X-Ray Diffraction Analysis

A Shimazu-GX-II type diffractometer was used in the conditions of 35 kvp., 15 ma., Ni-filtered Cu($K\alpha$) target, exposure time 1 hr. For taking a rotation diagram, the polymer specimen was rotated around the crystal axis at ca. 1 rpm.

III. RESULTS

β-Propiolactone

β-Propiolactone (I) has a melting temperature of −33.4°C.



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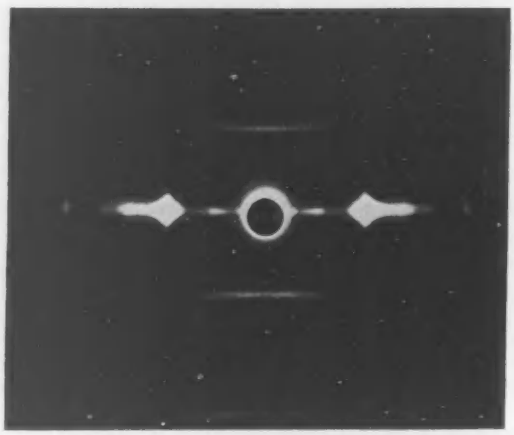


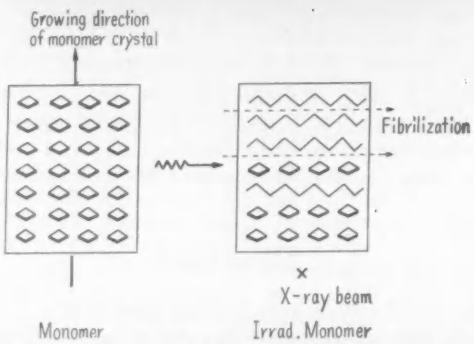


Fig. 1. X-ray diffraction diagram of poly-β-propiolactone. Nonrotation diagram.

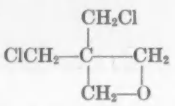
A large plate form of solid, 2 × 1.5 × 0.2 mm., can be crystallized by cooling of purified liquid β-propiolactone at ca. −36°C. Irradiation with γ-rays at the dosage of 2×10^5 *r* at −78°C., polymer (polyester in this case) gives yields of up to ca. 10%. After the extraction of unreacted monomer, the x-ray diffraction diagram was obtained (Fig. 1).

X-ray beam for diffraction analysis was inserted from the perpendicular direction to paper space.

The fiber axis of polymer molecules in the crystal lies perpendicular to the growing axis of the monomer crystal. Fibrilization occurs along the direction of polymer molecules. The fiber period is calculated here as 4.65–4.72 A. (avg. 4.69 A.) from the layer line in the x-ray diffraction diagram shown in Figure 1. The calculated fiber period of this polyester was 4.85 A., as estimated from the planar zigzag structure. The addition of γ-butyrolactone, methanol, and diketene to β-propiolactone changes the direction of the axis of polymer molecules in crystals obtained by solid-state polymerization.[9]

3,3-Bischloromethylcycloxabutane

3,3-Bischloromethylcycloxabutane (II) has a melting point of +18°C.



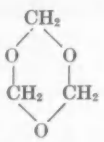
(II)

Poly-3,3-bischloromethylcycloxabutane is obtained in solid state by γ-irradiation to a dose of 6×10^5 *r* at 0°C., with a yield of ca. 60%. After the removal of unreacted monomer, the x-ray diffraction diagram shown in Fig. 2 was obtained.

Here the direction of polymer molecules in monoclinic solid is found to incline fixed angle 20–50° against each of three axes of monomer crystallite. As shown in Figure 2, a twin structure is observed in x-ray diagram having an angle of ca. 60° between two directions of each fiber axis. Solid-state polymerization of 3,3-bischloromethylcycloxabutane produces α-type[10] polyester having a planar zigzag chain configuration with an estimated fiber period of 4.82 A.

Trioxane

Trioxane (III), trioxymethylene has a melting temperature of +64°C. and hexagonal crystal form.



(III)

Polyoxymethylene (polytrioxane in this case) of high molecular weight is obtained by the solid-state radiation-induced polymerization of triox-

ane at 30–55°C. The direction of polymer molecules in polyoxymethylene obtained here is the same as the growing axis of the monomer crystal and it coincides also with the axis of fibrilization of polymer solid. In the x-ray diffraction analysis, the direction of the beam is perpendicular to the fiber axis of the polymer. The x-ray photograph taken on a fixed specimen shows unsymmetrical diffraction spots as shown in Figure 3.[11]

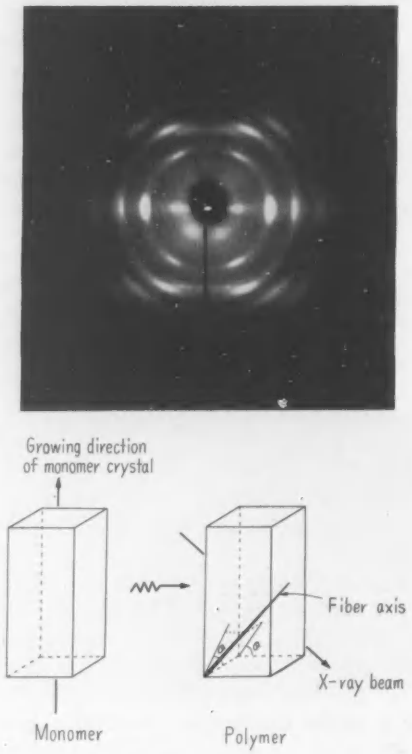


Fig. 2. X-ray diffraction diagram of poly-3,3-bischloromethylcycloxabutane. Rotation diagram.

The x-ray diagram taken by rotating the polymer specimen around the axis of polymer molecules is highly symmetrical (Fig. 4). As shown in Figure 4, a twin structure of polymer crystallites is observed in x-ray diagram having two directions or orientation at an angle of ca. 60°. Figure 5 shows the dependence of the formation of twin structure on the polymerizing temperature.

The index of all spots shown in these x-ray diagrams is almost the same as that of polyoxymethylene obtained in liquid state as reported by Tadokoro[8] except for that twin structure. The intensity of the anomalous spot

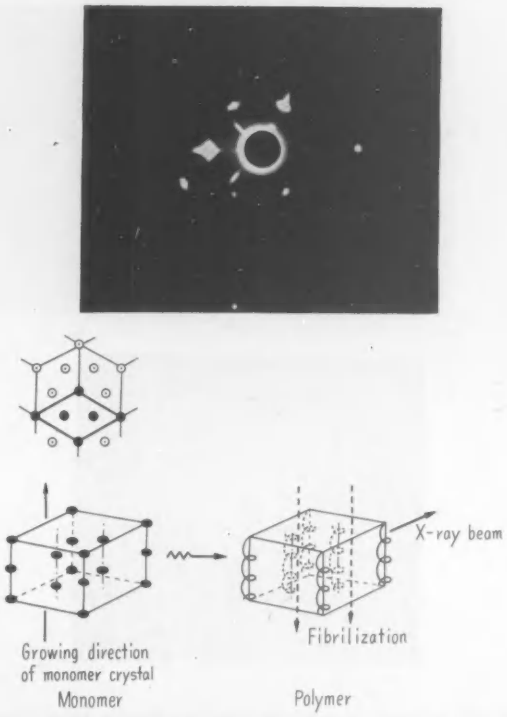


Fig. 3. X-ray diffraction diagram of polytrioxane. Nonrotation diagram.

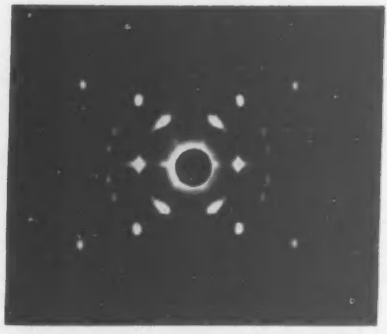


Fig. 4. X-ray diffraction diagram of polytrioxane. Rotation diagram.

indexed as that of the twin crystal decreases clearly on heat treatment at 170°C. for 2 and 5 hr. as shown in Figure 6.

A weight loss of about 30% is observed on heat treatment at 170°C. for 5 hr. (Fig. 6c).

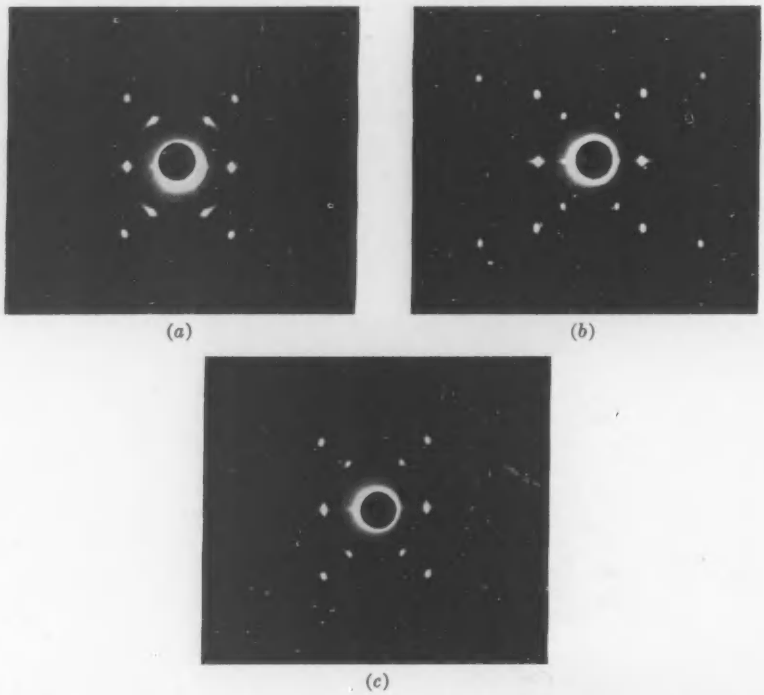
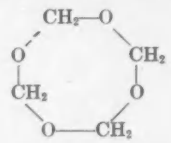


Fig. 5. X-ray diffraction diagram of polytrioxane showing twin structure at various polymerization temperatures: (*a*) 30°C.; (*b*) 45°C.; (*c*) 55°C. Rotation diagram.

Tetraoxane

Tetraoxane (IV), tetraoxymethylene has a melting point of +120°C., and is a needlelike crystal, having monoclinic crystal form.



(IV)

On irradiation to a dosage of ca. 4.5×10^5 *r* at 80°C., the monomer crystal is converted in about 94% yield into polyoxymethylene (polytetraoxane in this case) having a reduced viscosity number of ca. 0.5. The effect of polymerization temperature on the x-ray diffraction diagrams of polymer obtained in solid-state radiation-induced polymerization was examined and is shown in Figure 7.

As seen in Figure 7, the twin structure of polymer crystallites is observed slightly in the case of low temperature (60°C.) polymerization but not at high temperature (100°C.).

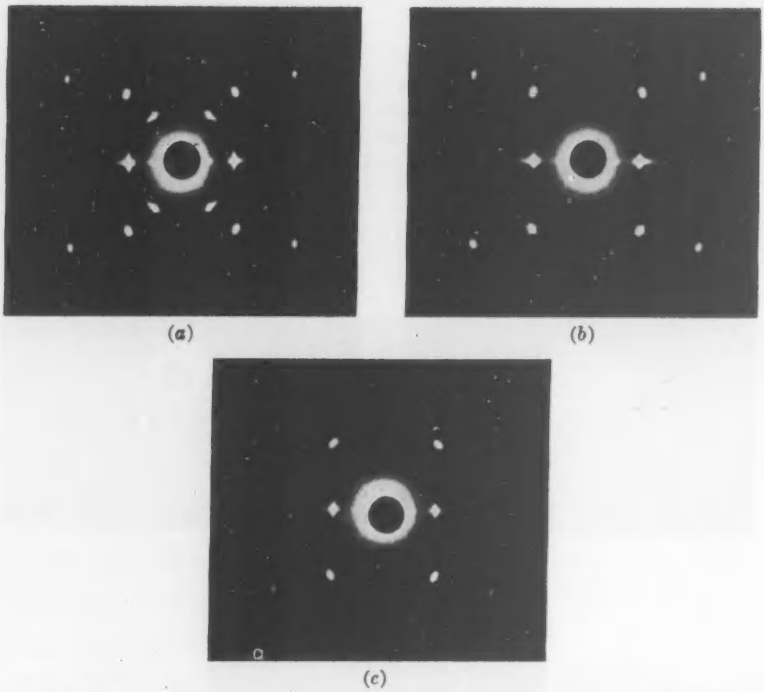


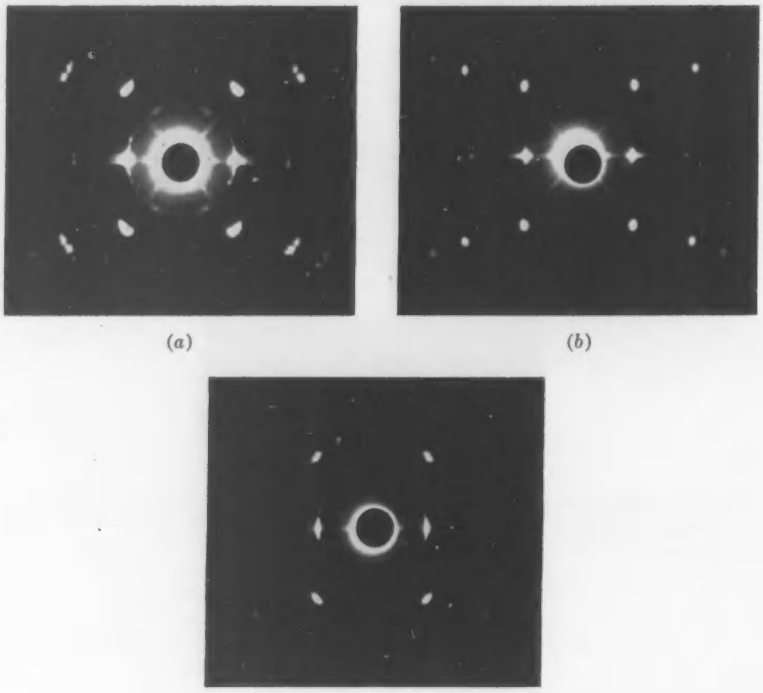
Fig. 6. X-ray diffraction diagram of polytrioxane showing effect of heat treatment on anomalous spots: (*a*) no heat treatment; (*b*) 170°C., 2 hr.; (*c*) 170°C., 5 hr. Rotation diagram.

IV. DISCUSSION

In the solid-state polymerization of 3,3-bischloromethylcycloxabutane, trioxane, and tetraoxane induced by γ-irradiation, the structure of the polymer obtained from the monomer crystals was estimated by X-ray diffraction analysis. It was clearly shown to be a three-dimensionally (trioxane and tetroxane) or one-dimensionally (3,3-bischloromethylcycloxabutane) oriented mosaic structure of twin crystals. The characteristics of those four-, six-, and eight-membered cyclic monomers seem to be symmetrical structure and high polymerizability without marked shrinkage of volume produced by the ring-opening polymerization. This twin structure was not observed in the diagram of polymer obtained from β-propiolactone, the monomer of which has an unsymmetrical chemical structure.

Poly-β-propiolactone and poly-3,3-bischloromethylcycloxabutane obtained by the solid-state radiation-induced polymerization had planar zigzag structures, with fiber periods of 4.69 and 4.82 A., respectively. In these cases, the axes of polymer molecules in polymer solids could not

coincide with the growing axes of monomer crystallites. Two kinds of polyoxymethylene obtained by solid-state radiation-induced polymerization, from trioxane and tetraoxane had the same helical structure, with fiber periods of 17.3 A. in both cases. The axis of polymer molecules in the polymer solid coincided well with the growing axis of monomer crystallite and also with the fibrilization axis of the polymer solid.



(*a*) (*b*)

(*c*)

Fig. 7. X-ray diffraction diagram of polytetraoxane obtained at various polymerization temperatures: (*a*) 60°C.; (*b*) 80°C.; (*c*) 100°C. Rotation diagram.

The direction of propagation in solid-state polymerization was found to be strongly determined by the arrangement of monomer molecules in the crystalline solid. Actual movement of monomer molecules in the crystal will be one of the most interesting subjects for studying in the solid-state polymerization of cyclic monomers induced by high energy radiation.

The authors would like to express appreciation to Drs. K. Kobayashi, Kyoto University, H. Tadokoro, Osaka University, Mr. T. Matsumoto, Kanebo Spinning Co., Mr. H. Maeda and Mr. H. Ochi, Toyokoatsu Co., who provided discussion, help, and encouragement.

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Synopsis

The structure of polymer obtained by γ-radiation-induced solid-state polymerization was examined by x-ray diffraction analysis. The polymers of 3,3-bischloromethylcycloxabutane, trioxane and tetraoxane were shown to have an oriented mosaic structure of twin crystallites, of which two polymers of oxymethylene were in helical configuration. The polymer of β-propiolactone was not in the twin crystal form. Two kinds of polymers obtained from β-propiolactone and 3,3-bischloromethylcycloxabutane were found to be in planar zigzag configuration.

Résumé

On étudie par analyse aux rayons-X la structure du polymère obtenu par polymérisation à l'état solide, induite par les rayons-gamma. Les polymères du 3,3-bischlorométhylcycloxabutane, trioxane, et tétraoxane possèdent une structure tridimensionnelle en mosaïque orientée de cristallites jumeaux dans laquelle deux polymères d'oxyméthylène présentent une configuration hélicoïdale. Le polymère de β-propiolactone n'est pas sous la forme d'un cristal double. Les deux sortes de polymères obtenus à partir de la β-propiolactone et du 3,3-bischlorométhylcycloxabutane ont une configuration planaire en zig-zag.

Zusammenfassung

Die Röntgen-Strukturanalyse eines durch γ-Strahl-induzierte Polymerisation in fester Phase erhaltenen Polymeren wurde durchgeführt. Die Polymeren von 3,3-Bischlormethylcyclo-oxabutan, Trioxan und Tetroxan besassen eine dreidimensional orientierte Zwillingskristallit-Mosaikstruktur, wobei zwei Oxymethylenpolymere eine Helixkonfiguration aufwiesen. Das β-Propiolactonpolymere bildete keinen Zwillingskristall. Zwei, aus β-Propiolacton und 3,3-Bischlormethylcyclo-oxabutan erhaltene Polymere hatten eine ebene Zickzack-Konfiguration.

Discussion

H. Morawetz (*Polytechnic Institute, Brooklyn, N. Y.*): Are the monomers which you copolymerized in solid solution isomorphous? Do you believe that these solid solutions prepared by shock cooling represented equilibrium systems?

S. Okamura: We have now preliminary results on the determination of melting points in the mixtures of those four systems. At this moment it seems from the melting points and composition-curves that no equilibrium is reached.

H. Cherdron (*Sté. Shell, Germany*): It is known from trioxane polymerization that the degree of crystallinity of the resulting polyoxymethylenes depends on how the polymers have been prepared. Thus, solution- or melt-polymerization leads to lower degrees of crystallinity than polymerization in the solid state. Similar observations have been made in the case of *p*-propiolactone, but in contrary to trioxane, there are also differences in the melting point between the polymers which come out of solution- and of solid-state polymerization (85°C. and 125°C., respectively). Do you think that this is due to differences in the degree of crystallinity or eventually to differences in the crystal structure of the polymers?

S. Okamura: In the case of the solution ionic polymerization of β-propiolactone the low molecular weight polyester has been expected to be obtained for the possibility of chain transfer reaction. Solid-state polymerization might be suitable to form high molecular weight and thus high melting point polymer.

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Effect of Polymorphism in Solid-State Polymerization

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INTRODUCTION

Solid-state reactions in general may be influenced by two inherent properties of a compound, its chemical constitution and its crystallography. Although it is often difficult experimentally to separate and assess the magnitude of each factor, an approach becomes feasible when the compound exhibits polymorphism, the ability to exist in two or more crystalline modifications. In the case of such compounds, although all polymorphic modifications are chemically identical, each will possess different physical properties such as melting point, vapor pressure, solubility, refractive index, etc., reflecting the differences in the arrangement of molecules in the solid-state.[1] Such differences must also be expected to influence the solid state polymerization behavior of a monomer. Although recent reviews of solid state polymerization by Garratt[2] and Magat[3] state that the effect of some crystallographic aspects of the monomer have been considered, no study has been reported of the effect of polymorphism.

Tributylvinylphosphonium bromide, $[CH_2{=}CHP(C_4H_9)_3]^+Br^-$, was found to be capable of existing in three monotropic polymorphic modifications, forms I, II, and III. Form II, although thermodynamically unstable at atmospheric pressure, could be obtained in a metastable condition over a wide temperature range which permitted a comparative study of the polymerization behavior of it with the stable form I. The results of this study are presented below.

EXPERIMENTAL AND RESULTS

Radiation Sources

X-Rays were generated by a 250 kvp. x-ray machine (General Electric Maxitron-250) operated at 6–30 ma. with a 1 mm. copper filter. The output of the machine was constant within 3–5%. Dosimetry was conducted by means of the Fe^{++}–Fe^{+++} system. Different dose rates were achieved by varying the current while the sample remained a fixed distance from the target, or by varying the distance while the voltage and current were held constant. The energy absorption by the system was transformed from ferrous sulfate values in the aqueous system using the mass absorption

coefficients at 150 k.e.v. for the aqueous and our systems, ignoring any contribution from photoelectric effect.[4] The values shown in the content of this paper are those based on Fe^{++}–Fe^{+++} dosimetry unless specified as the energy absorbed by the monomer system.

Material

Tributylvinylphosphonium bromide was prepared according to the method described by Hoffman.[5] It was recrystallized twice from a mixture of ethyl acetate and acetonitrile.

Characterization of Polymorphs

Microscopy. Three polymorphs of tributylvinylphosphonium bromide have been observed, although only two have been isolated for characterization. When a small quantity of the compound was melted between slide and cover glass and observed microscopically as crystallization occurred, the melt usually supercooled below its normal freezing point and an unstable polymorph nucleated and grew. The most unstable form (III) of the three polymorphs was seen infrequently as a crystal front growing through the melt. Form III invariably transformed immediately after crystallization and a transformation front of III → II or III → I followed closely behind the crystal front of III. Most frequently form II crystallized directly from the supercooled melt assuming a preferred orientation showing low order polarization colors and a BX_a interference figure with rather diffuse isoggres. $2E$, measured by Mallard's method[6] on centered BX_a figures was about $+36°$ $(-)$. The transformation rate of form II → form I was very slow below about 40°C., and once obtained on a slide in the absence of form I nuclei, form II could be retained as such in a metastable condition indefinitely. Small samples of form II often resisted transformation even when heated on a hot stage, and a melting point of 149.3°C. was measured in this manner. The stable form I could be obtained by crystallization from the melt at temperatures near the melting point, 154.3°C., or by solid–solid transformation of form II → form I induced by warming a preparation of form II. Crystallization from acetonitrile–ethyl acetate mixture at 0°C. always produced form I. Optical examination of single crystals of form I showed them to be orthorhombic, with refractive indices (589 mμ, 25°C.) $\alpha = 1.520 \pm 002$, $\beta = 1.536 \pm 002$, $\gamma = 1.538 \pm 002$, $2V$ (calculated from α, β, γ) $= 52°$, optic sign $= (-)$, strong dispersion $V > r$. Fusion preparations of forms I and II were most easily distinguished from each other by conoscopical estimation of $2E$. Forms I and II could be obtained in the same preparation by proper manipulation as illustrated in the photomicrograph of Figure 1. The more birefringent form I is located in the center and is surrounded by the less birefringent form II. Figures 1*b* and 1*c* show the solid–solid transformation of form II into form I as the temperature was raised.

Infrared Absorption. Crystals of both forms I and II were grown from the melt between sodium chloride plates (0.01 spaces) and identified microscopically. Their infrared absorption spectra were obtained by using a Beckman IR-4 spectrometer (NaCl optics). The pertinent parts of the spectra are reproduced in Figures 2*a* and 2*b*. Differences in intensities among close lying bands were found and are indicated by dotted lines under the bands. This type of difference could result from either different orientations of the same crystalline modification or from polymorphism.

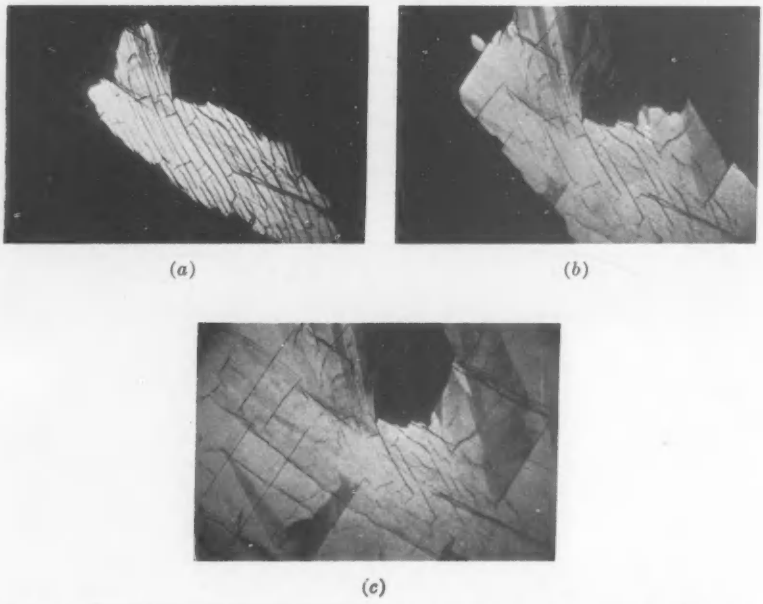
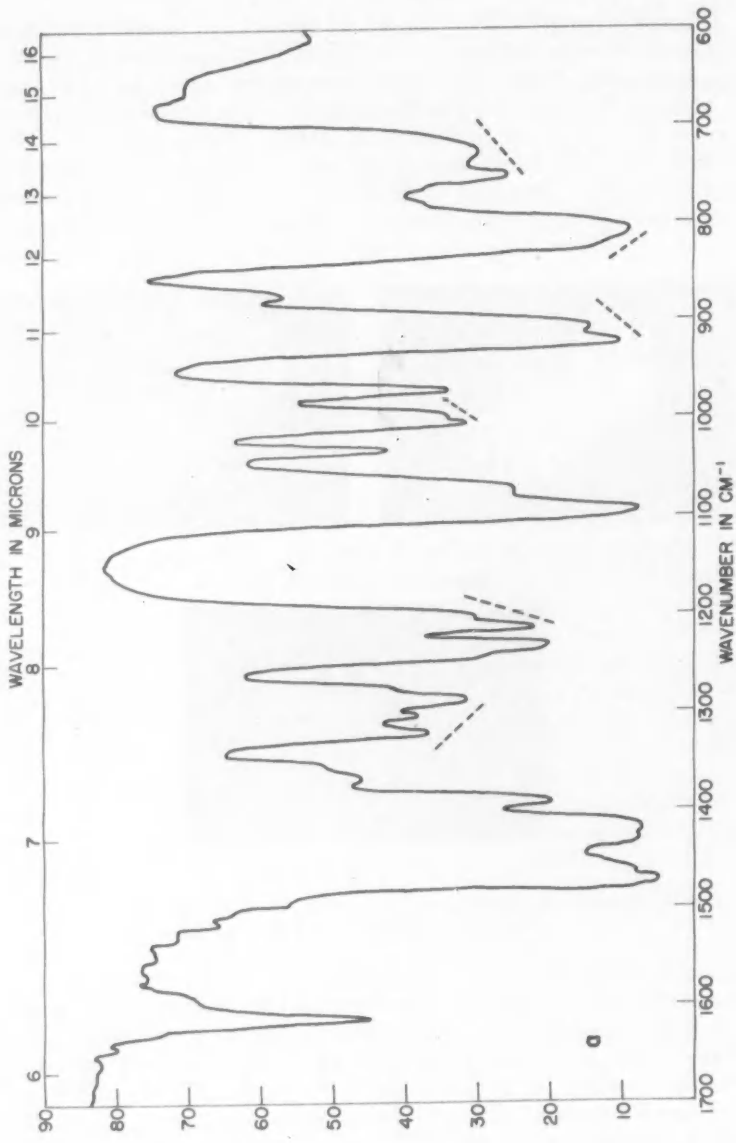


Fig. 1. Polymorphic transformation of tributylvinylphosphonium bromide: (*a*) room temperature; (*b*) ca. 85°C.; (*c*) ca. 100°C.

Inasmuch as the preparations had been identified microscopically as polymorphic forms I and II, the differences in the spectra are believed to be characteristic of the two polymorphs when grown from the melt in the manner described.

X-Ray Diffraction. The x-ray diffraction powder pattern of form I was easily obtained and is given in Table I. Form II invariably transformed to form I during grinding preparatory to loading into a capillary, so that its powder pattern could not be obtained. Attempts to obtain significant x-ray data by diffractometer techniques on thin films of forms I and II crystallized from the melt were unsuccessful because of preferred orientation of the crystals.


WAVELENGTH IN MICRONS
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WAVENUMBER IN CM⁻¹
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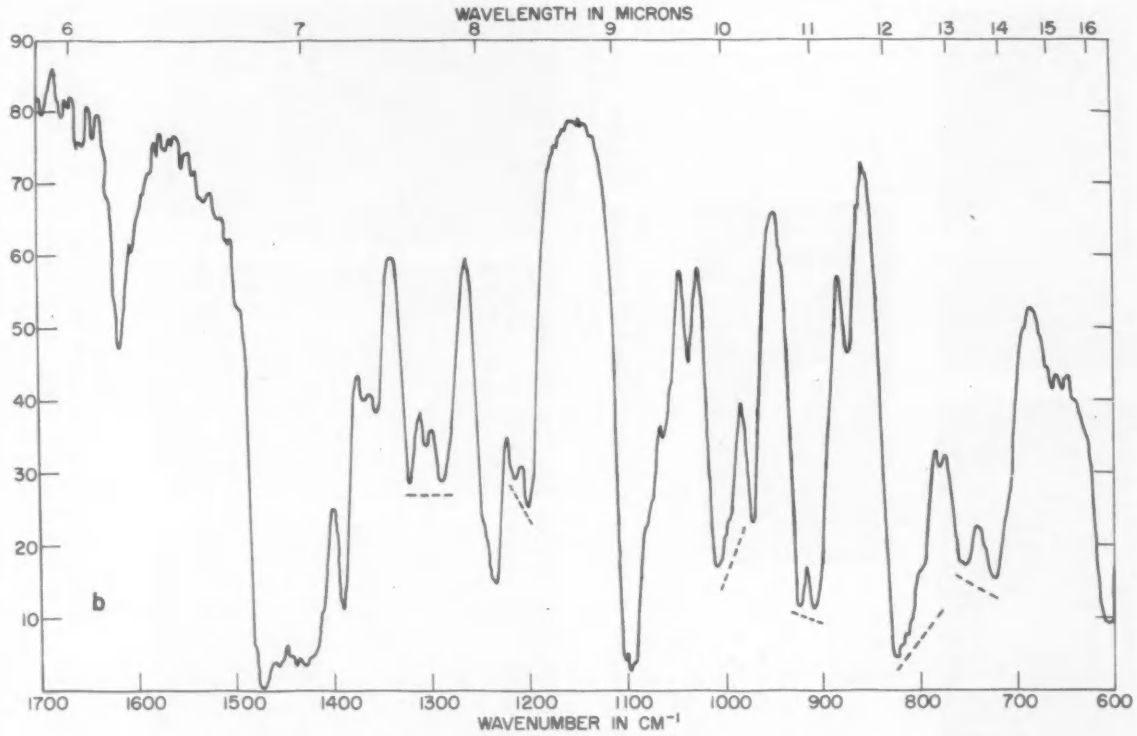


Fig. 2. Partial infrared spectra of tributylvinylphosphonium bromide: (*a*) crystal form I; (*b*) crystal form II.

TABLE I
X-Ray Powder Diffraction Data of Tributylvinylphosphonium Bromide at $2\theta = 5$–$40°$

I	d, A.	I	d, A.
2	15.0	4	3.83
10	11.2	4	3.72
4	9.30	2	3.57
3	7.76	4	3.35
1	7.08	8	3.24
5	6.23	3	3.13
1	5.94	5	3.06
5	5.40	4	2.84
1	5.21	1	2.70
4	4.90	1	2.60
4	4.69	2	2.54
4	4.44	1	2.48
3	4.27	1	2.41
3	4.19	1	2.37
7	4.02	1	2.27

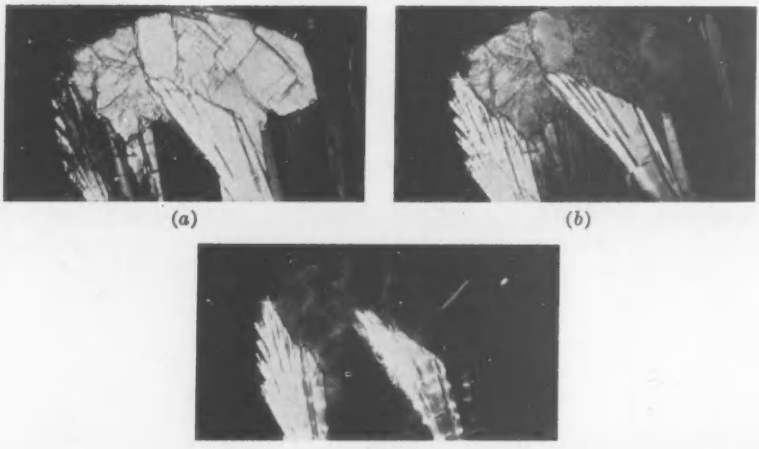
Sample Preparation and Method of Following Kinetics

Samples of both polymorphs were most conveniently prepared for optical examination and polymerization studies by recrystallization from the melt between small fragments of slide and cover glass. Several such preparations were put into a Pyrex optical cell which was evacuated and sealed off for studies in vacuum. For studies in air a drying tube was affixed to the cell so as to avoid water condensation when working at low temperatures. Unless specified otherwise, the polymerizations were carried out in vacuum. Specific crystals in each sample preparation were selected and located with respect to include bubbles, characteristic shrinkage cracks, or other morphological characteristics of the preparation. The optical retardation of these crystals was measured by means of a Berek compensator initially and after successive doses of radiation.

A single crystal of a monomer when viewed microscopically between crossed polars exhibits a polarization color determined by its retardation, R, which is a function of its birefringence, B, and its thickness, l.

$$R = Bl$$

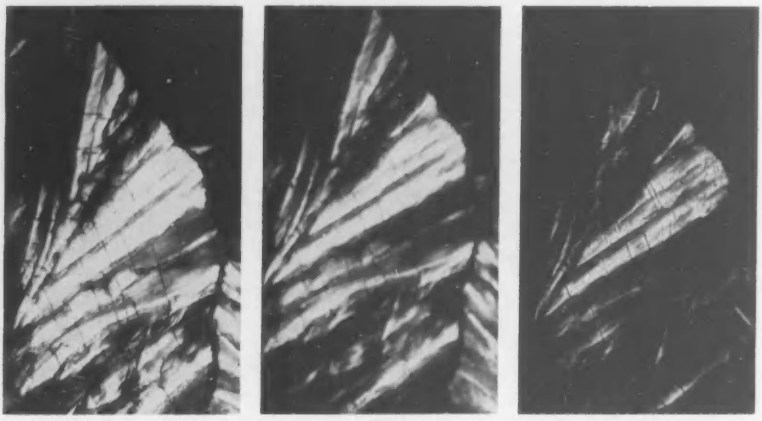
Since the birefringence of a given monomer is determined by its crystal lattice, it will remain unchanged as the crystal polymerizes except for such strains as may be introduced by the polymerization process. When the crystalline monomer is converted into amorphous polymer, an effective decrease in thickness of the remaining monomer results. This is reflected in a decrease in optical retardation, and consequently in the polarization color of the crystal. Figures 3*a*, 3*b*, and 3*c* and Figures 4*a*, 4*b*, and 4*c* show crystals of forms I and II, respectively, undergoing x-ray-induced polymerization. The retardation decreases as polymerization proceeds.



(a) (b)

(c)

Fig. 3. Photomicrographs of tributylvinylphosphonium bromide I undergoing polymerization: (a) monomer before irradiation; (b) partly polymerized; (c) nearly completely polymerized. Crossed polars.



(a) (b) (c)

Fig. 4. Photomicrographs of tributylvinylphosphonium bromide II undergoing polymerization: (a) monomer before irradiation; (b) partly polymerized; (c) nearly completely polymerized. Crossed polars.

It was observed experimentally that the polymerization proceeded at an equal rate in three perpendicular directions through crystals of form I (see next section). Therefore, the weight or volume fraction of a crystal converted to polymer was calculated as $(R_0^3 - R_t^3)/R_0^3$, where R_0 is the retardation of the crystal measured before radiation, and R_t is the retardation after irradiating for a time t.

Radiation-Induced Polymerization

Effect of Temperature. The polymerization of form I was investigated at 60, 45, 30, 0, and −80°C. The results are presented in Figure 5. At

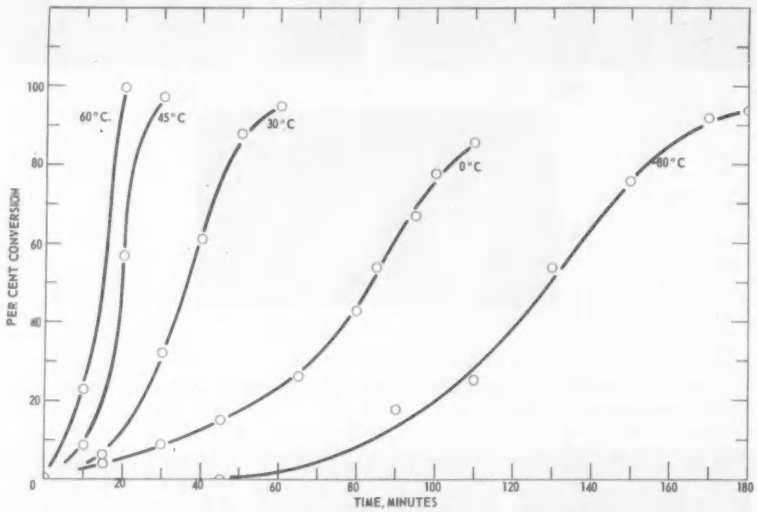


Fig. 5. Polymerization of tributylvinylphosphonium bromide, crystal form I, at different temperatures at a dose rate of 0.28 Mrad/hr.

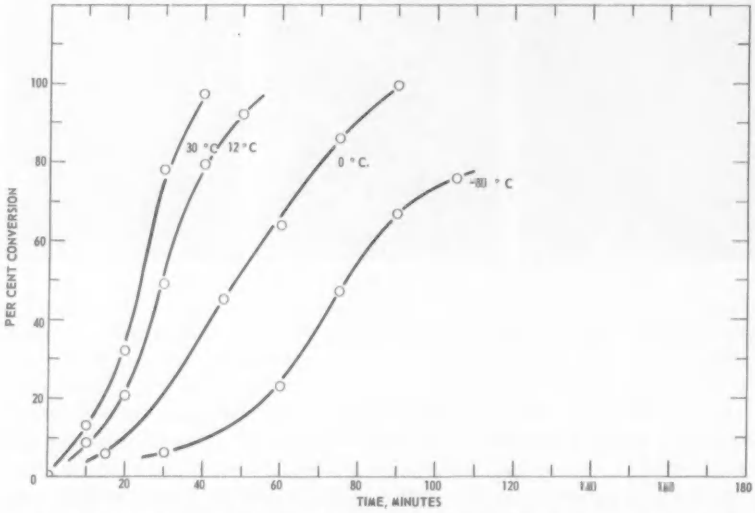


Fig. 6. Polymerization of tributylvinylphosphonium bromide, crystal form II, at different temperatures at a dose rate of 0.28 Mrad/hr.

temperatures above 60°C. the polymerization was very fast. It was also observed that the polymerization took place in the melt. The polymerization of form II was carried out at 30, 12, 0, and −80°C. The results are shown in Figure 6. Above 30°C. form II tends to transform to form I, although slowly; therefore, its polymerization was not studied above that temperature. The per cent polymerization versus time or total dose curves (dose rate = 0.28 Mrad/hr.) are S-shaped for both polymorphs.

Effect of Polymorphism. The results indicate that form II polymerizes faster than form I under all the experimental conditions investigated. Table II is a summary of the time required for 50% polymerization ($t_{1/2}$)

TABLE II
Polymerization of Tributylvinylphosphonium Bromide

Crystal Form	Dose rate (and energy absorbed), Mrad/hr.[a]	Temperature, °C.	$t_{1/2}$ min.[b]	G Value at 50% conversion[c]
I	0.28[a] (0.63)	60	15.0	9872
"	"	45	20.0	7425
"	"	30	36.3	4093
"	"	0	83.4	1781
"	"	−80	129.5	1147
"	0.56 (1.26)	30	14.5	5120
"	0.17 (0.38)	"	44.4	5546
"	0.14 (0.32)	"	46.2	6329
II	0.28 (0.63)	30	24.0	6188
"	"	0	49.0	3031
"	"	−80	77.0	1928
"	0.56 (1.26)	30	9.4	8235
"	0.17 (0.38)	"	32.3	7623
"	0.14 (0.32)	"	31.0	9441

[a] Based on Fe^{++}–Fe^{+++} dosimetry.
[b] Time required for 50% conversion.
[c] Based on energy absorbed by the system.

under different conditions. Figure 7 is a plot of log $(10^3/t_{1/2})$ versus $10^3/T$ and Figure 12 is a plot of log $(10^3/t_{1/2})$ versus log dose rate. Except for the relatively faster rates of form II, the two polymorphs seem to behave similarly towards temperature and dose rate. The effect of polymorphism is also represented in Figure 11.

Effect of Crystal Orientation. Polymerization rates were measured on crystals lying in three perpendicular orientations: BX_a, BX_0 and ON, which were recognized by conoscopical observation. The results are shown in Figure 8 where the polymerization was carried out at −80°C. at a dose rate of 0.28 Mrad/hr. It is indicated that, within experimental error, the polymerization proceeded essentially at the same rate along all three directions.

Effect of Thickness of the Crystal. Polymerizations of crystals of the same orientation but different in thickness were studied at 0°C. at a dose

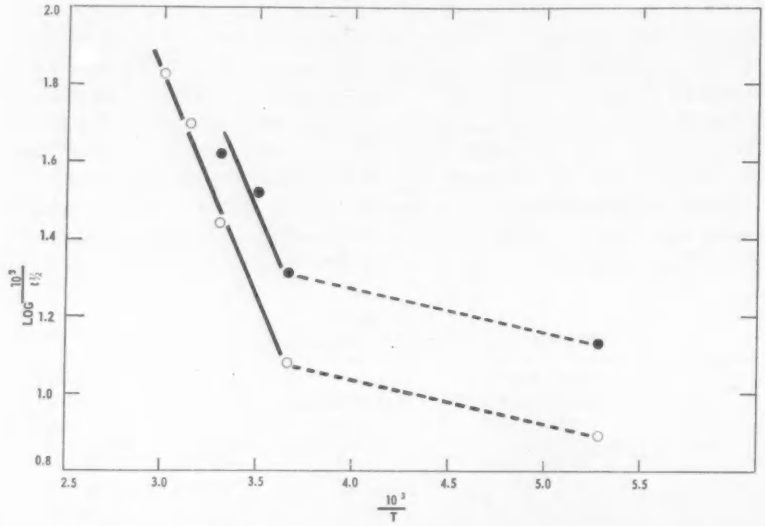


Fig. 7. Arrhenius plot for polymerization of tributylvinylphosphonium bromide at a dose rate of 0.28 Mrad/hr.: (○) crystal form I; (●) crystal form II.

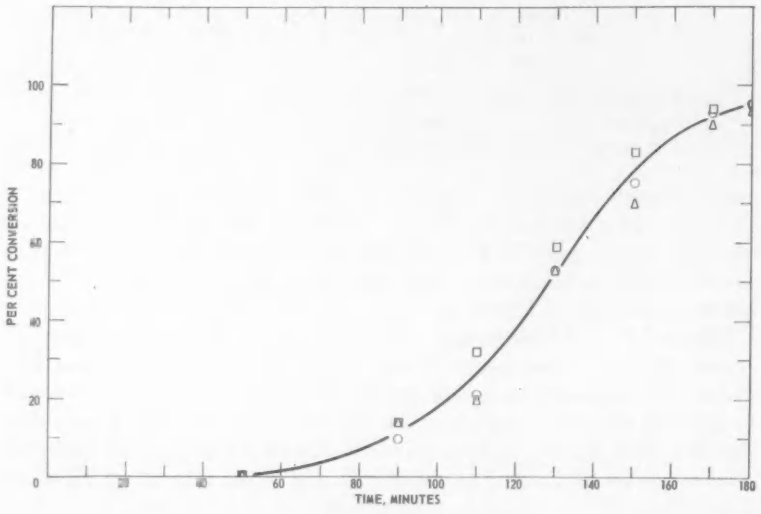


Fig. 8. Polymerization rates along three different orientations of the crystals for polymerization at −80°C. at a dose rate of 0.28 Mrad/hr.: (○) BX_a; (△) BX_b; (□) ON.

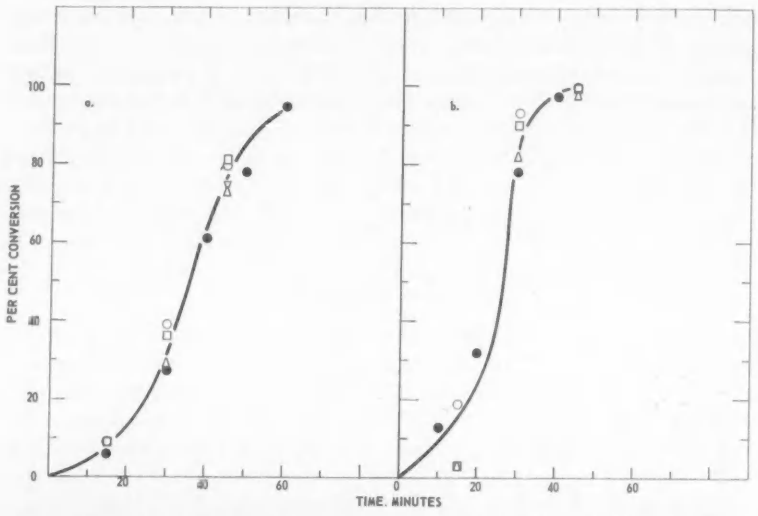


Fig. 9. Effect of thickness of the crystals on the rate of polymerization of tributylvinylphosphonium bromide at 30°C. and a dose rate of 0.28 Mrad/hr.: (*a*) form I, (○) R_0 = 628 mμ; (□) 508 mμ (●) 344 mμ, (△) 329 mμ, (▽) 161 mμ; (*b*) form II, (○) R_0 = 1538 mμ, (●) 1012 mμ (□) 1006 mμ, (△) 526 mμ.

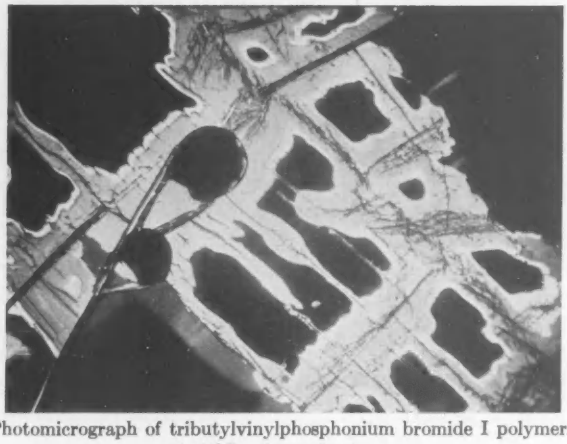


Fig. 10. Photomicrograph of tributylvinylphosphonium bromide I polymerized in air at 30°C. Crossed polars.

rate of 0.28 Mrad/hr. The results are shown in Figure 9. The variation in thickness is indicated by the difference in the original optical retardation of the crystals. The rates of polymerization were essentially the same in crystals of several fold variation in thickness.

Effect of Oxygen. The polymerizations of both forms I and II were investigated at 100, 30, 0, and −80°C. in air. It was observed that at

30°C. and above the polymerization took place only in the centers of the crystals, as shown in Figure 10. At 0°C., the polymerization appeared to proceed uniformly through the crystals. The rates of polymerization of both forms I and II were higher than those obtained in vacuum under

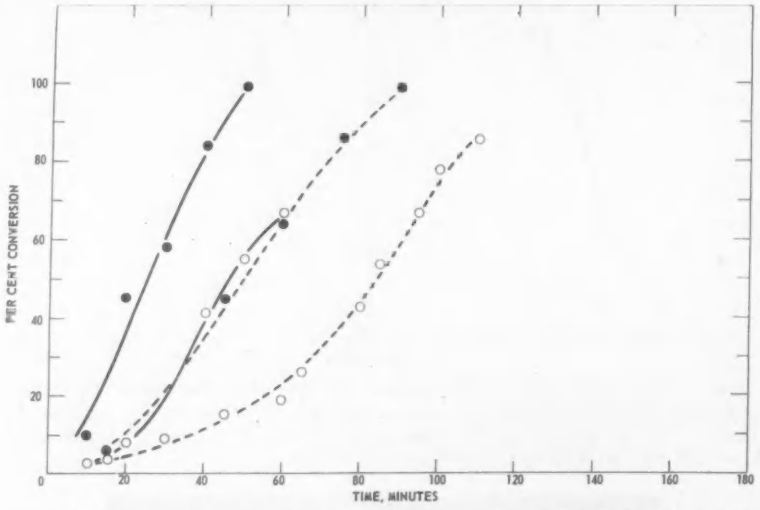


Fig. 11. Effects of oxygen and of polymorphism on the polymerization of tributylvinylphosphonium bromide at 0°C. and a dose rate of 0.28 Mrad/hr.: (O) form I; (●) form II; (–) polymerization in vacuum; (——) polymerization in air.

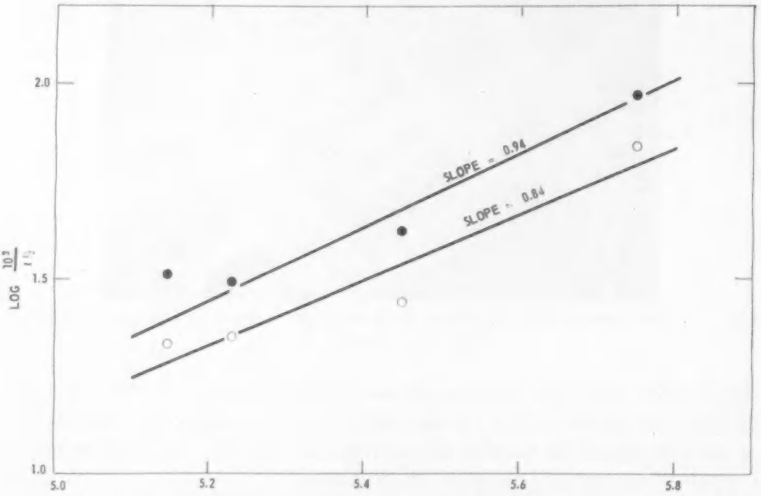


Fig. 12. Dose rate dependence of polymerization of tributylvinylphosphonium bromide at 30°C.: (O) crystal form I; (●) crystal form II.

otherwise the same conditions. The results are compared in Figure 11, where the dotted and solid curves represent the polymerization in vacuum and in air, respectively. At −80°C., no polymerization took place in either form I or II after 150 min. of irradiation at 0.28 Mrad/hr.

Effect of Dose Rate. The dose rate dependence at 30°C. of the rate of both forms I and II was examined at four different dose rates: 0.14, 0.17, 0.28, and 0.56 Mrad/hr. The plots of log $(10^3/t_{1/2})$ versus log dose rate are presented in Figure 12. The slopes of the least square lines for forms I and II are 0.84 and 0.94, respectively.

Electron Spin Resonance

The electron spin resonance investigation was carried out on unirradiated monomer (form I grown from solution) and polymer; and on monomer and polymer irradiated by x-ray and by 253.7 mμ ultraviolet light. A Varian 100 kcycle spectrometer was used. The results showed: (*1*) no ESR signal was detected from unirradiated monomer or polymer; (*2*) monomer and polymer irradiated with a low dose (5.0×10^4 rads) at liquid nitrogen temperature gave a signal at that temperature showing poorly resolved hyperfine structure, and this signal decayed within a space of minutes at room temperature; (*3*) monomer and polymer irradiated with 1×10^6 rads at room temperature showed spectra with poorly resolved hyperfine structure. Over a period of days the spectra decayed slowly and it became obvious that there were at least two radicals in both monomer and polymer systems. Also in both systems the radical which showed hyperfine structure decayed more quickly than another species whose spectrum was probably a single broad line. There were differences between the spectra of irradiated monomer and polymer. The most striking difference was the occurrence of two peaks ~130 gauss apart in the irradiated monomer which were absent in the irradiated polymer. Ultraviolet-irradiated (253.7 mμ) monomer and polymer gave a single sharp line at $g \cong 200$ and this was stable at room temperature. In one monomer sample, irradiated for 17 hr. while surrounded by 6 Westinghouse Sterilamp bulbs (253.7 mμ) two weak peaks were seen evenly spaced about the center line and 132 gauss apart. It would be reasonable to ascribe this pair of peaks to hyperfine interaction with the phosphorus atom. However, practically no polymer was formed in this monomer sample (Iodine no.: before radiation = 81.5; after radiation = 77.4).

Characterization of Polymers

Molecular Weight. Since all the kinetic studies were carried out microscopically, molecular weight determinations were conducted on different samples. Five-gram samples of form I crystals were sealed in ampules under a vacuum of 10^{-3}–10^{-4} mm. Hg and irradiated under various conditions. The results are summarized in Table III. After irradiation the monomer–polymer mixture was dissolved immediately in water and

TABLE III
Data on Molecular Weights and Properties of Polytributylvinylphosphonium Bromide

Polymerization temp., °C.	Total polymerization time, min.[a]	$[\eta]^{30}_{0.3M\ LiBr}$, dl./g.	$M_w \times 10^{-4}$	T_g, °C.	T_t, °C.		T_{10}, °C.	
					In air	In N_2	In air	In N_2
0	120	0.128	5.0	5	340	340	396	396
30	30	0.149	4.8					
"	60	0.149	5.5					
"	120	0.150	5.4	16 ± 2	330	330	389	405
"	180	0.151	7.4					
"	330	0.163	9.6					

[a] Dose rate = 1.5 Mrad/hr. by Fe^{++}–Fe^{+++} dosimetry; 3.4 Mrad/hr. absorbed. Essential complete polymerization in all cases. Loss of low molecular weight material through dialysis: 5–20%.

dialyzed in casein tubes until no bromide was detected outside the tubes. This usually took two days. The polymer solution was then freeze-dried and the polymer was obtained as a white powder. Both light-scattering molecular weights and intrinsic viscosities were measured in 0.3*M* aqueous lithium bromide solution.

Properties of the Polymers. The polymer obtained from form I is soluble in water. It is hygroscopic. The glass transition temperature and thermostability as determined by differential thermoanalysis ranges from T_g: 5–16°C.; T_t 340°C. in air or N_2; T_{10}: 396°C. in air, 396–411°C. in N_2.

Polymer resulting from polymerization of form II has not been obtained in sufficient quantity for characterization.

DISCUSSION

In the present investigation of solid state polymerization of tributylvinylphosphonium bromide, the observed conversion–time curves (Figs. 5 and 6) are similar to those reported by Baysal et al., for acrylamide.[7] In both cases the polymerization can be carried essentially to completion and there is an acceleration in rate with increased conversion. In both cases the polymers formed are amorphous. These results represent nonsteady-state polymerization kinetics, and a nucleation mechanism for acrylamide has been suggested.[7,8] A rate expression has been formulated by Baysal et al. as the following:

$$\log (M_0/M) = (k_p k_i f I/4.606)t^2$$

In the case of acrylamide, when $\log M_0/M$ is plotted against t^2 a straight line is obtained for the initial reaction (first 20%), and a second straight line of higher slope is obtained after the initial reaction. When our results are plotted in the same manner, as shown in Figure 13 for the crystal form I and Figure 14 for the crystal form II, sets of similar plots are obtained.

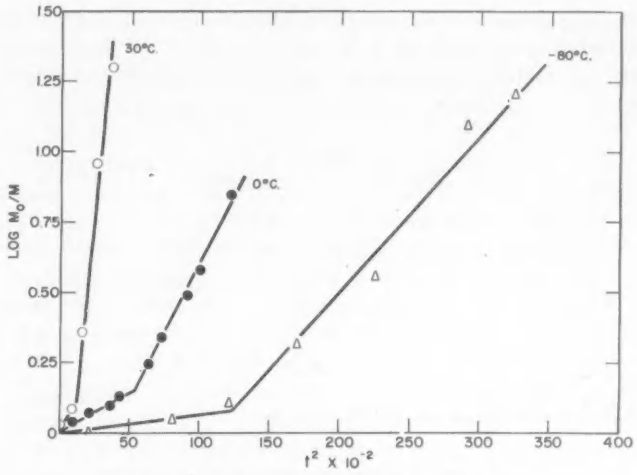


Fig. 13. Polymerization of crystal form I.

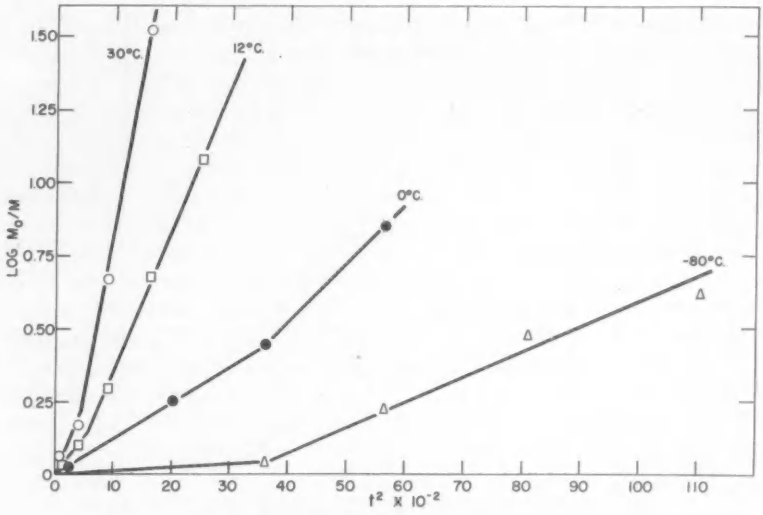


Fig. 14. Polymerization of crystal form II.

Here the straight lines of lower slopes represent up to 30% conversion. In the polymerization of form I at 45 and 60°C., due to the fast nature of the reaction, the data (see Fig. 5) are not sufficient to permit definite plots of this type. Also, in the plot representing the polymerization of crystal form II at −80°C. in Figure 14, insufficient data are available to define the slope of the initial reaction. The values of $k_p k_i f I/4.606$ calculated from the slopes

of the initial reactions for the rest of the experiments are tabulated in Table IV. Arrhenius plots for both forms based on the available data are given in Figure 15. Similar values of activation energy (0–30°C.) are obtained for both forms.

TABLE IV
Rate of Initial Polymerization

Crystal form	Temp., °C.	Dose rate I, Mrad/hr.	$\frac{k_p k_i f i \times 10^4}{4.606}$	$\frac{k_p k_i f \times 10^{10}}{4.606}$	$-\Delta E_a$, kcal./mole
I	30	0.28	1.64	5.86	
"	0	"	0.43	1.54	7 (0–30°C.)
"	−80	"	0.12	0.43	
II	30	0.28	4.05	14.5	
"	12	"	2.41	8.61	
"	0	"	1.24	4.43	6.5 (0–30°C.)

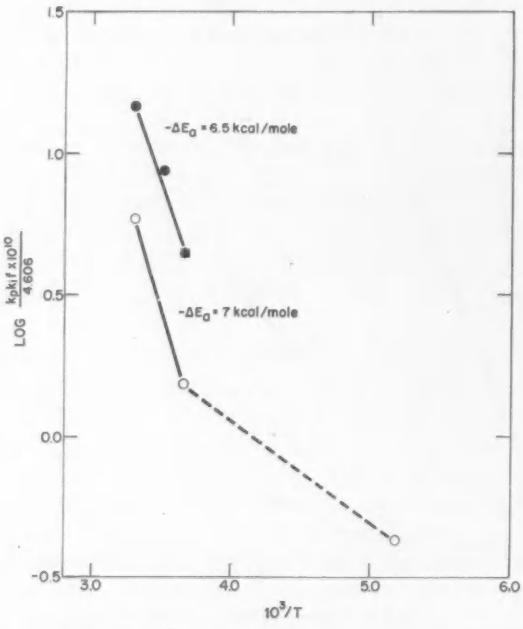


Fig. 15. Arrhenius plots: (○) crystal form I; (●) crystal form II.

As another means of comparing the effect of temperature on the overall reactions, time to complete 50% conversion of monomer to polymer ($t_{1/2}$) was taken as an index of polymerization rate. Half-times were chosen as an index since in all experiments this point included both the initial slow and subsequent rapid periods of the polymerization. Plotting the reciprocal

of these half-times versus reciprocal temperatures produces a plot analogous to that obtained for the Arrhenius equation. As indicated in Figure 7, again, it becomes apparent that the two plots have essentially the same slopes but different intercepts. This again indicates that the energy term is similar for the polymerization of both forms.

If the energy term is indeed similar for the polymerization of both forms, the difference in rate would arise primarily from the difference in steric and collision factors. This is entirely reasonable for the system under investigation since the two crystal forms are chemically identical, but have different crystal structures. In the case of form II the steric and collision factors must be more favorable for polymerization than in form I.

In the present case, the unstable form II polymerizes at faster rates than the stable form I under all the experimental conditions employed. However, the direction of differences in polymerization rates as a result of polymorphism cannot be generalized. Effects other than rate differences, such as tacticity and polymorphism of the resulting polymer, also might be expected when crystalline polymers are obtained from different polymorphs of monomer. Further investigations along this line should prove to be significant and interesting.

Polymerization of tributylvinylphosphonium bromide in vacuum, as shown in the photomicrographs (Figs. 3 and 4) appears to take place uniformly throughout the crystals. This does not necessarily contradict the heterogeneous nature of the polymerization, since a high nucleation rate forming large numbers of microscopically unresolved nuclei would produce an appearance of gross homogeneity. However, the propagation could still be proceeding heterogeneously on a submicro scale.

The lack of difference in rates of polymerization along different directions through the crystals of form I (see Fig. 8) suggests that the monomer molecules occupy a variety of orientations within the unit cell.

It is difficult to make definite conclusions as to the mechanism of the polymerization of tributylvinylphosphonium bromide in the solid state. The fact that oxygen inhibits the polymerization at 30°C. or above (Fig. 10) indicates that the reaction is free radical in nature at such temperatures. However, ESR studies show that free radicals are formed under the influence of ultraviolet light, but these radicals do not induce polymerization. The free radicals produced by ultraviolet light, however, are different from those produced by x-rays. The observations that the polymerization of both forms is accelerated by oxygen at 0°C. (Fig. 11) but inhibited by oxygen at −80°C. are surprising, and no reasonable explanation can be offered at the present time. In the plots of Figures 7 and 15 there is indication of a change of slope as the temperature is lowered from 0 to −80°C. Since all the temperatures indicated are well below the melting point of both forms of the monomer, and since no other solid–solid transition has been observed in this temperature range, the change in slope in these Arrhenius-type plots might indicate some change of mechanism (free radi-

cal, ionic, etc.). Polymerization at temperatures between 0 and −80°C. is being investigated further.

The dependence of polymerization rate on dose rate in both forms is well in accordance with the values obtained for solid state polymerization in general, and indicates that the termination is essentially unimolecular. Dose rate dependence was calculated by using half-times as polymerization rate indices, since insufficient data were available on the initial portions of the conversion–time curves to obtain enough rate constants for this purpose. The molecular weight data were obtained after complete polymerization and so do not furnish information on the dependence of molecular weight on total dose during polymerization. The results (Table III) show that: (*1*) polymers obtained at 0 and 30°C. have the same molecular weights (rows 1–4); (*2*) continuous radiation after complete polymerization increases the molecular weight (rows 4–7); (*3*) in all cases a portion, ranging from 5 to 20% of low molecular weight material which is permeable to casein, is obtained.

CONCLUSIONS

The most important result of this investigation has been the demonstration that polymorphism is a factor which must be considered in solid state polymerizations. This observation, although not surprising, is highly significant. It points out that monomer involved in any study should be characterized crystallographically before its polymerization behavior is investigated, since most organic, as well as inorganic compounds can exist in two or more crystalline modifications. It has been reported[2,3] that the "size and quality" of monomer crystals have effects on solid state polymerization. However, it should be noted that the conditions under which small or imperfect crystals are usually obtained also favor the formation of unstable polymorphs. Therefore, unless the crystals are characterized, the effect of polymorphism might very well be mistaken for that of crystal size or quality. For example, no effect of crystal size on polymerization rate was observed for either polymorph of tributylvinylphosphonium bromide in this investigation.

In the polymerization of tributylvinylphosphonium bromide, the two crystalline modifications investigated behave similarly kinetically with regards to the shape of their conversion–time curves and their values of dose rate dependence. They also polymerize by the same mechanism as indicated by the nature of inhibition and acceleration by oxygen and by the effect of temperature. The faster rates in the crystal form II are attributed primarily to the steric and collision factors which are governed by the crystalline structure.

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Synopsis

The influence of polymorphism of the monomer in solid state polymerization has been demonstrated by comparing the polymerization behavior of two crystalline modifications of tributylvinylphosphonium bromide. Both modifications were found to polymerize at fast rates to give amorphous polymers, and the unstable modification to polymerize faster than the stable modification under all the experimental conditions investigated. Both crystalline modifications appeared to polymerize by the same mechanism and follow the same kinetics as evidenced by the nature of inhibition and acceleration by oxygen, by their conversion–time curves, and by their dose rate dependence. The overall activation energies for the polymerization were found to be the same for both forms. The faster rates of the unstable form are attributed primarily to the steric and collision factors in the Arrhenius equation, which are governed by the crystal structure of the two polymorphs. The rate of polymerization was determined to be independent of crystal size. The stable form was found to polymerize at equal rates in all crystallographic directions.

Résumé

On a démontré l'influence du polymorphisme d'un monomère sur la polymérisation à l'état solide, en comparant la polymérisation de deux formes cristallines du bromure de tributylvinylphosphonium. On constate que les deux formes polymérisent à une vitesse élevée, donnant des polymères amorphes, lors de toutes les conditions expérimentales étudiées, les formes instables polymérisent plus vite que les formes stables. Les deux formes cristallines semblent suivre la même cinétique et le même mécanisme de polymérisation; cela est mis en évidence par les courbes conversion-temps, la nature de l'inhibition et de l'accélération par l'oxygène, et par la dépendance vis-à-vis des doses d'irradiation. On trouve la même énergie d'activation globale pour les deux formes. La vitesse plus élevée de la forme instable est attribuée surtout aux facteurs stériques et aux facteurs de collision de l'équation d'Arrhénius, qui sont déterminés par la structure cristalline des deux formes polymorphes. On trouve que la vitesse de la polymérisation est indépendante de la grandeur ces cristaux. La forme stable polymérise à des vitesses égales dans tous les directions cristallographiques.

Zusammenfassung

Durch einen Vergleich des Polymerisationsverhaltens zweier kristalliner Modifikationen von Tributylphosphoniumbromid wurde der Einfluss der Polymorphie des Monomeren auf die Polymerisation in festem Zustand nachgewiesen. Beide Modifika-

tionen polymerisieren mit hoher Geschwindigkeit und ergeben amorphe Polymere, u. zw. polymerisierte die instabile Modifikation unter allen untersuchten experimentellen Bedingungen schneller als die stabile. Beide kristallinen Modifikationen polymerisieren offenbar nach demselben Mechanismus und folgen derselben Kinetik, wie durch die Art der Inhibierung und Beschleunigung durch Sauerstoff, durch ihre Umsatz-Zeit-Kurven und die Abhängigkeit von der Dosisleistung bewiesen wird. Die Bruttoaktivierungsenergie der Polymerisation ist für beide Formen gleich gross. Die höhere Geschwindigkeit der instabilen Form wird in erster Linie dem sterischen und dem Stossfaktor in der Arrhenius-Gleichung zugeschrieben, die durch die Kristallstruktur der beiden polymorphen Formen bestimmt werden. Die Polymerisationsgeschwindigkeit ist von der Kristallgrösse unabhängig. Die stabile Form polymerisiert in allen kristallographischen Richtungen mit gleicher Geschwindigkeit.

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Copolymerization in Solid Solutions

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INTRODUCTION

It has been demonstrated that polymerizations of monomers in the solid state are influenced by their crystallography.[1,2] As a result, monomer reactivities are different from those in homogeneous liquid media. It can be visualized that in the solid state the copolymerization behaviors of monomer pairs will be different from those in the liquid state also. The crystallography should have effects on the rates, structure of the copolymer, and the reactivity ratios of the monomers. However, quantitative studies of copolymerization in the solid state will be limited to monomers which are isomorphous. It has been found that tributylvinylphosphonium bromide is isomorphous with tributylvinylphosphonium iodide. This communication describes the characterization of their solid solutions and their polymerization behaviors.

EXPERIMENTAL AND RESULTS

Material

Tributylvinylphosphonium bromide was prepared according to the procedure described by Hoffman.[3] Tributylvinylphosphonium iodide was prepared from the bromide by means of ion exchange. A brief procedure is described below. Dowex-1 ion-exchange resin was packed in a column and conditioned by passing through three cycles of 1*N* KOH and 1*N* HCl. The amount of acid and base used was calculated to be 3–4 times in excess of the capacity of the ion-exchange resins. Each time after the acid or the base, excess water was passed through the column until the effluent was neutral. Finally, acetone was passed through to wash off any organic impurity in the resins. The column was re-equilibrated with water. Excess amount of 1*N* KI solution was then passed through, followed by excess H_2O until the effluent was free of iodide. A solution of tributylvinylphosphonium bromide, equivalent to $^1/_3$ of the capacity of the resins, was then passed through at a rate such that total exchange was obtained. The column was eluted with water. The solution of tributylvinylphosphonium iodide was collected as the effluent. After evaporation of water,

tributylvinylphosphonium iodide was obtained as pure, colorless crystals, m.p. 102.0°C.

Characterization of Solid Solutions

Phase Diagram. The phase diagram of tributylvinylphosphonium bromide/iodide was determined by microscopical fusion methods.[4] The characterization of the polymorphs of the bromide has been reported previously.[5] The iodide may crystallize spontaneously as either form I or form II; a third form which is nearly isotropic has been observed very infrequently. When the iodide crystallizes as form II it usually transforms spontaneously to form I. Form II can sometimes be obtained in a metastable condition at room temperature, but invariable transforms to I if warmed slightly above room temperature. Solid solutions are formed between the stable polymorphs of each compound and also between the unstable polymorphs of each compound. Such behavior is described as parallel isodimorphism.[6]

The solidus and liquidus curves of the I-I and II-II solid solutions have been determined for eight compositions containing various amounts of bromide: 0, 27.9, 41.1, 49.7, 75.8, 85.0, 96.5, and 100 mole-% Br^-. The results are represented in Figure 1. The points shown are believed to be accurate to ±3°C.

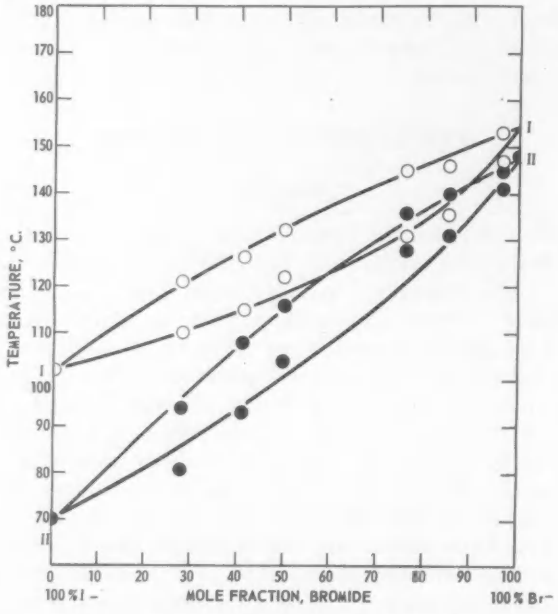

Fig. 1. Phase diagram of tributylvinylphosphonium bromide–tributylvinylphosphonium iodide.

TABLE I
X-Ray Powder Diffraction Data for Solid Solutions of Tributylvinylphosphonium Bromide/Iodide

100% Br^-		27.9% Br^-–72.1% I^-		49.7% Br^-–50.3% I^-		75.8% Br^-–24.2% I^-		100% I^-	
I	*d*, A.	*I*	*d*, A.	*I*	*d*, A.	*I*	*d*, A.	*I*	*d*, A.
2	15.0	2	14.7	1	14.7	2	14.7	1	15.0
10	11.2	10	10.8	10	10.9	10	9.82	10	10.9
4	9.30	4	9.20	5	9.20	6	9.20	5	9.20
3	7.76	2	7.69	2	7.69	3	7.62	2	7.69
1	7.08	1	7.07	1	7.08	1	7.02	2	7.13
5	6.23	4	6.28	4	6.19	5	6.19	4	6.32
1	5.94			1	5.90	1	5.82		
		4	5.53	4	5.47			5	5.60
5	5.40					5	5.43		
1	5.21			1	5.09	1	5.12		
		3	4.95					3	4.98
4	4.90			3	4.90	5	4.87		
		3	4.77					2	4.82
4	4.69			3	4.72	4	4.67		
								3	4.55
4	4.44	4	4.48	4	4.46	5	4.44		
3	4.27								
3	4.19	6	4.19	4	4.21	4	4.19		
								8	4.11
7	4.02	6	4.04	6	4.02				
						8	3.98	1	3.97
4	3.83								
		6	3.77	5	3.77	6	3.78	5	3.78
4	3.72								
								5	3.70
		1	3.62					1	3.64
2	3.57			1	3.60	1	3.54		
		1	3.44			1	3.46	1	3.48
4	3.35	8	3.32					8	3.35
				8	3.29			1	3.30
8	3.29					6	3.25		
3	3.13	4	3.10	4	3.10	2	3.13	4	3.12
5	3.06					3	3.06		
		2	2.89	2	2.90	1	2.92	3	2.92
4	2.84					1	2.84		
				1	2.81			1	2.79
1	2.70	1	2.74	1	2.72	2	2.70		
		2	2.63	2	2.63	2	2.62	2	2.66
1	2.60	1	2.56	1	2.57				
2	2.54					1	2.55		
1	2.48					1	2.48	1	2.48
1	2.41			1	2.43	1	2.42		
		1	2.37	1	2.37	1	2.35	1	2.37
		1	2.31					1	2.30
1	2.27	1	2.28	1	2.27	1	2.27		
		1	2.18			1	2.18	1	2.19
		4	2.13			2	2.13		

X-Ray Diffraction Studies. Powder patterns of the pure iodide and the solid solutions of the compositions described above were obtained. The results summarized in Table I indicate that the bromide and the iodide form continuous solid solutions.

Radiation Source and Dosimetry

The radiation source and dosimetry employed were the same as described previously.[5] The energies absorbed by the present systems were, however, more complicated, since they contained both bromide and iodide. Therefore, at the same machine output, each system absorbed different amounts of energy. For quantitative comparison of the polymerization rates, each system should be corrected to a common dose rate taking into account the mass absorption of the two components and the rate dependence on dose rate. Since the dose rate dependence was determined for the pure bromide and the pure iodide only, no attempt was made to correct the rates of polymerization of the mixtures to a common dose rate. The variation in energy absorption would be a maximum of 20%, the pure iodide being the highest. The activation energies were compared directly among the different solid solutions of the bromide and the iodide, since activation energy is independent of the dose rate. The dose rates specified are based on Fe^{++}–Fe^{+++} dosimetry.

Polymerization

The polymerization studies were carried out in the same manner as described previously.[5] The copolymerization was first investigated qualitatively employing mixed fusion technique. As shown in the photomicrograph in Figure 2*a*, on one side of the preparation is the pure bromide and on the opposite side the pure iodide; in between the pure monomers are the solid solutions of varying compositions. After successive radiation at 0°C., it was observed that the iodide was the first to become completely polymerized. After the bromide had polymerized completely, solid solutions of some compositions remained only partially polymerized. This series of events is shown in photomicrographs in Figures 2*b* and 2*c*.

Polymerization rates were then determined quantitatively on tributylvinylphosphonium iodide (I) and six solid solutions of the bromide (I) and iodide (I) containing, respectively, 27.9, 41.4, 49.7, 75.8, 85.0, and 96.5 mole-% bromide. Figure 3 summarizes the results obtained on eight compositions, ranging from the pure iodide to the pure bromide at 60, 30, 0, −80°C., and in some cases at 45°C. S-shaped curves are obtained in all cases when per cent conversion is plotted against time. It was observed that the polymerization could proceed to completion in all cases. Again, as an index for polymerization rate,[5] the time required for 50% conversion ($t_{1/2}$) for each composition at different temperatures is tabulated in Table II. Figure 4 represents the effect of temperature where, log ($10^3/t_{1/2}$) is plotted against $10^3/T$. For clarity in presentation, the plots are arbitrarily

divided into four pairs. The points obtained at −80°C. lie above the extrapolated straight line obtained from the points at 60 to 0°C. The deviation becomes greater as the solutions become richer in bromide. Apparent activation energies from 0 to 60°C. were calculated from the slopes of the least squares lines (Fig. 4). The values are recorded

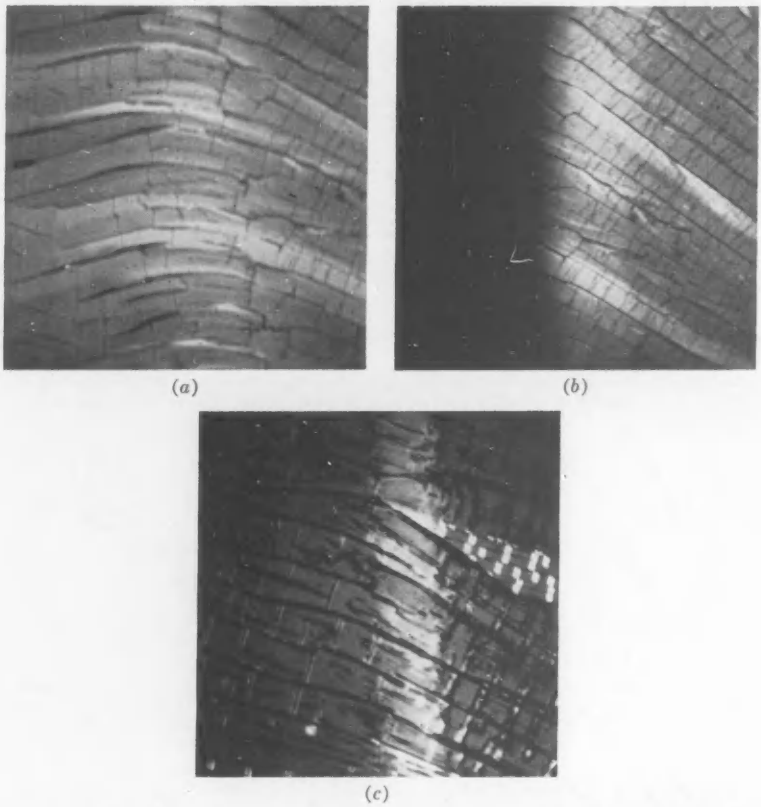

Fig. 2. Photomicrographs showing polymerization of a mixed fusion of tributylvinylphosphonium bromide (right) and tributylvinylphosphonium iodide (left): (*a*) monomers before polymerization; (*b*) iodide completely polymerized, bromide partly polymerized; (*c*) iodide and bromide completely polymerized but some compositions of mixed crystals remain only partly polymerized. Photographed with crossed polars and (*c*) with first-order red compensator to show amorphous regions.

in Table II. The polymerizations between 0 and −80°C. are currently under investigation. The dependence of rate on dose rate for tributylvinylphosphonium iodide was determined at four different dose rates: 0.14, 0.17, 0.28, and 0.56 Mrad/hr. The slope of the least squares line of the plot of log $(10^3/t_{1/2})$ versus log dose rate is 0.84.

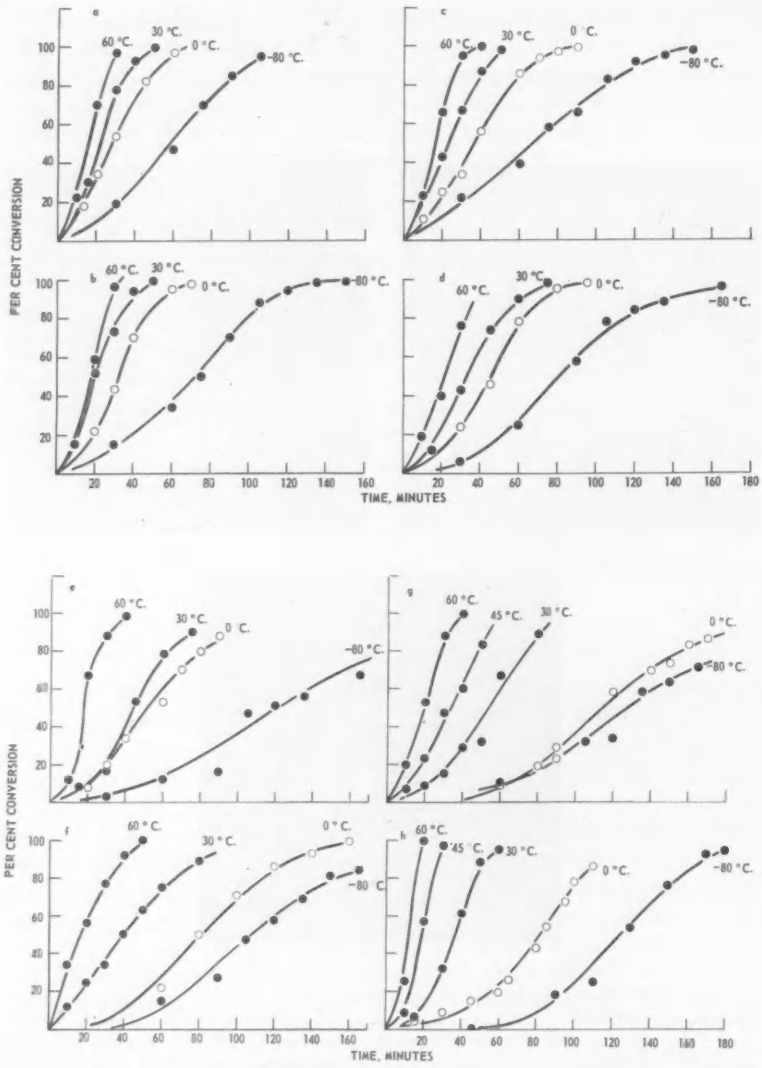

Fig. 3. Polymerization of solid solutions of tributylvinylphosphonium bromide and iodide at different temperatures and at a dose rate of 0.28 Mrad/hr. (Fe^{++}–Fe^{+++} dosimetry): (*a*) 0% Br–100% I; (*b*) 27.9% Br–71.1% I; (*c*) 41.1% Br–58.9% I; (*d*) 49.7% Br–50.3% I; (*e*) 75.8% Br–24.2% I; (*f*) 85.0% Br–15.0% I; (*g*) 96.5% Br–3.5% I; (*h*) 0% Br–100% I.

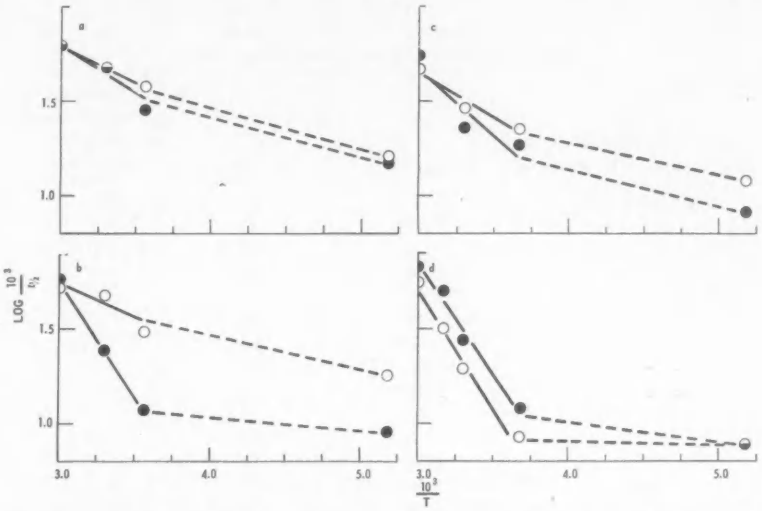

Fig. 4. Effect of temperature on conversion of various mixtures: (*a*) (O) 0% Br–100% I, (●) 37.7% Br–62.3% I; (*b*) (O) 27.9% Br–72.1% I, (●) 85.0% Br–15.0% I; (*c*) (O) 49.7% Br–50.3% I, (●) 75.8% Br–24.2% I; (*d*) (O) 96.5% Br–3.5% I, (●) 100% Br–0.0% I.

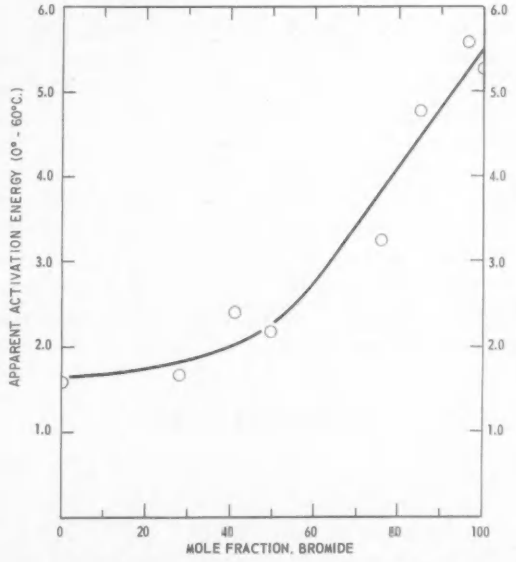

Fig. 5. Relationship between apparent activation energy and mole fraction.

TABLE II
Polymerization of Solid Solutions of
Tributylvinylphosphonium Bromide and Iodide

Composition mole-% Br^-[a]	Temp., °C.	$t_{1/2}$, min.	Apparent activation energy (0–60°C.), kcal./mole
0 (100% I^-)	60	16	
	30	21	
	0	27	1.6
	−80	62	
27.9	60	19	
	30	21	
	0	33	1.7
	−80	75	
41.1	60	16	
	30	21	
	0	35	2.4
	−80	67	
49.7	60	21	
	30	34	
	0	44	2.2
	−80	83	
75.8	60	18	
	30	44	
	0	54	3.3
	−80	122	
85.0	60	17	
	30	41	
	0	85	4.8
	−80	112	
96.5	60	18	
	45	32	
	30	51	
	0	121	5.6
	−80	127	
100	60	15	
	45	20	
	30	36	
	0	83	5.3
	−80	130	

[a] At dose rate = 0.28 Mrad/hr. by Fe^{++}-Fe^{+++} dosimetry. Energy absorbed increases as the amount of iodide increases.

Inhibition by Oxygen

When the polymerizations were carried out in air as described previously,[5] it was observed that: (*1*) at 30°C., in the pure iodide and in all solid solutions, polymerization only took place in the center of the crystals; (*2*) at 0°C. the iodide appeared to polymerize evenly throughout the crystals up to 25% conversion, but at a slower rate than that in vacuum;

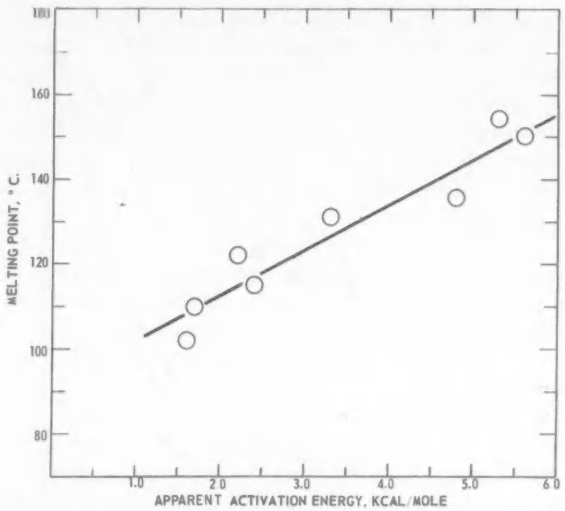

Fig. 6. Relationship of melting points of tributylvinylphosphonium bromide–iodide solid solutions and apparent activation energies for their polymerization.

(3) at −80°C., no polymerization took place in the iodide after 190 min. radiation at 0.28 Mrads/hr.

DISCUSSION AND CONCLUSIONS

Solid–solid solubility of tributylvinylphosphonium bromide and iodide over the entire composition range is indicated from the study of mixed fusions (Fig. 2*a*) and from the melting points determined on mixtures of known compositions (Fig. 1). Results of x-ray diffraction studies substantiate the existence of solid solutions over the composition range studied also (Table I). Based on these results, the rates of polymerization of the solid solutions were expected to be intermediate in between those of the pure bromide and the pure iodide, and the order of the polymerization rates to be dependent on the compositions of the solid solutions. However, the photomicrographs of the polymerization of a mixed fusion at 0°C. show that there are compositions which polymerize slower than either of the pure monomers (Figs. 2*a*, *b*, and *c*). Furthermore, when $t_{1/2}$ is plotted against composition at different temperatures, as shown in Figure 7, it is seen that at 0 and 30°C. slow polymerization rates occur at compositions in the vicinity of 96% bromide, while at 60 and −80°C. the rates are in the order as expected. These observations are difficult to explain. One possibility is the existence of crystallographic difference between the slow and other compositions which have not been revealed by the present work. Consequently, a more detailed examination of the phase diagram in the bromide-rich region is indicated, and is currently under investigation.

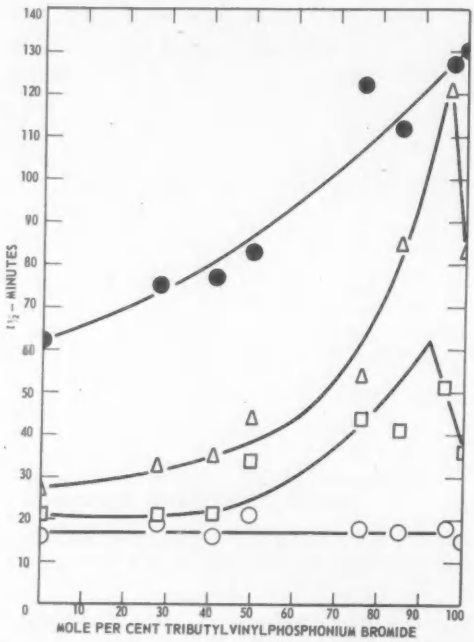

Fig. 7. Plots of $t_{1/2}$ vs. mole per cent Br^- for polymerization of solid solutions of tributylvinylphosphonium bromide and iodide at a dose rate of 0.28 Mrad/hr. (Fe^{++}–Fe^{+++} dosimetry): (●) 60°C.; (□) 30°C.; (△) 0°C.; (●) −80°C.

For the same reasons, the phase diagram and the polymerization behaviors in the iodide-rich region should be examined more critically, even though no abnormality has been indicated in that region by the present investigation.

The phase relationship between the unstable polymorphs of each compound has been presented here to show that their solid solutions also exist. The study of their polymerization is of importance and interest, but more difficult experimentally because of their tendency to transform into the stable modification. An investigation of their polymerization behavior will be undertaken at a later date.

The relative polymerization rates as represented by $t_{1/2}$ shown in Figure 7 indicate two trends: (*1*) at 60°C. all compositions polymerize at comparable rates; (*2*) at 30, 0, and −80°C., aside from the above-mentioned slow compositions at 0 and 30°C., the rate increases with the iodide contents. These results indicate that different compositions have different activation energies for polymerization. In Table II the values for apparent activation energy calculated from 0 to 60°C. show that it increases from the pure iodide to the pure bromide. Although extraordinary polymerization rates were found for the 96.5% Br^- composition, the value of its apparent activation energy was not outstanding. The plot of apparent

activation energy versus composition (Fig. 5) has the same shape as that of the solidus curve in the phase diagram (Fig. 1). These results are reasonable, since in melting the systems change from the crystalline state to the liquid state, and in the polymerization under investigation, the systems change from the crystalline state to an amorphous solid. In both cases, disruption of the crystal lattice is involved. If these two phenomena are related, the relationship should be demonstrable by a plot of heat of fusion versus activation energy for polymerization of different compositions. The heats of fusion have not been determined for the systems. Since they are directly related to the melting points, the melting points are plotted against the apparent activation energies in Figure 6. A fair linear relationship is indicated. The straight line was obtained by the method of the least squares. These results provide further evidence of the influence of crystallography on the rate of polymerization in the solid state. They, however, show a different type of effect from that caused by polymorphism in the pure bromide.[4] In the previous work the two polymorphs are chemically identical but different in crystal structure. These, however, have similar melting points (I: 154.3°C.; II: 149.3°C.). It was observed that the energy of activation for polymerization was essentially the same for both polymorphs. The difference in rate was ascribed primarily to steric factors arising from differences in the arrangement of the molecules in the crystals. Based on the present results it would be of interest to investigate a polymorphic system in which the polymorphs have substantially different melting points, for in such a system the energy of activation for polymerization might be expected to be different for the polymorphs also. In the present investigation, the systems are chemically different but crystallographically similar, therefore, polymerization differences must be accounted for primarily on a basis of chemical composition. As the results indicate the effect of composition on the polymerization is in a manner analogous to that of the melting behavior of solid solutions.

Referring to Figure 4, the deviation of the −80°C. points from the extrapolated line through the other points may represent a change in slope, and therefore a possible change in polymerization mechanism.[5] It is of interest that in the case of the pure iodide and iodide-rich compositions (27.9% Br^-–72.1% I^- and 37.7% Br–62.3% I^-), essentially straight lines can be drawn through the points representing the temperature range from 60 to −80°C. This observation together with the fact that oxygen inhibits the polymerization of the pure iodide differently than it does the bromide[5] suggests that there may be a difference in polymerization mechanism between the two monomers. More experiments are being carried out to elucidate this point.

The authors wish to express their gratitude to Dr. L. A. Siegel and Mr. William Doughman for their assistance in x-ray diffraction studies, and to Dr. D. J. Salley for his helpful suggestions.

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Synopsis

Tributylvinylphosphonium bromide has been found to be isomorphous with tributylvinylphosphonium iodide. Their solid solutions have been characterized microscopically and by x-ray diffraction. X-Ray-initiated polymerization of the pure iodide and copolymerization of six solid solutions of different compositions of the two monomers have been investigated over the temperature range from 60 to −80°C. S-shaped polymerization rate curves were obtained. Generally the polymerization rates of intermediate compositions were found to be intermediate between the two pure monomers. However, some compositions rich in the bromide exhibited slower rates than either pure monomers. The apparent activation energies for polymerization increased with increased bromide/iodide ratios, and in a manner analogous to the effect of composition on the melting behavior of the solid solutions.

Résumé

On a constaté que le bromure de tributylvinylphosphonium est isomorphe avec l'iodure de tributylvinylphosphonium. Leurs solutions solides ont été caractérisées microscopiquement et par diffraction des rayons-X. La polymérisation de l'iodure pur initiée par des rayons-X, et la copolymérisation de six solutions solides sont examinées dans un intervalle de températures de 60 à −80°C. On obtient des courbes de vitesses de polymérisation en forme de S. En général, on trouve que les vitesses de polymérisation de compositions intermédiaires sont intermédiaires entre celles des deux monomères purs. Cependant, certaines compositions riches en bromure montrent des vitesses plus faibles que celles des monomères purs. Les énergies d'activation apparentes des polymérisations augmentent avec une augmentation du rapport bromure/iodure, et cela d'une façon analogue à l'effet de la composition sur le comportement à la fusion des solutions solides.

Zusammenfassung

Tributylvinylphosphoniumbromid und Tributylvinylphosphoniumjodid sind untereinander isomorph. Ihre festen Lösungen wurden mikroskopisch und mittels Röntgenbeugung charakterisiert. Es wurde die durch Röntgenstrahlung gestartete Polymerisation des reinen Jodids und die Copolymerisation von sechs verschieden zusammengesetzten festen Lösungen der beiden Monomeren im Temperaturbereich zwischen 60 und −80°C untersucht. Dabei erhielt man S-förmige Polymerisationsgeschwindigkeits-Kurven. Die Polymerisationsgeschwindigkeit von Mischungen mittlerer Zusammensetzung lag zwar im allgemeinen zwischen denjenigen der beiden reinen Monomeren, bei Mischungen mit hohem Bromidgehalt waren jedoch die Geschwindigkeiten niedriger als bei jedem der beiden reinen Monomeren. Die scheinbare Aktivierungsenergie der Polymerisation nahm mit steigendem Bromid/Jodid-Verhältnis in einer dem Einfluss der Zusammensetzung auf das Schmelzverhalten der festen Lösungen analogen Weise zu.

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Radiopolymérisation de l'Acrylonitrile Solide: Éffet des Conditions de Cristallisation et des Transitions de Phase

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Nous avons poursuivi notre étude sur la radiopolymérisation de l'acrylonitrile (AN) solide[1–6] dans le but de connaître le rôle des transitions de phase sur la cinétique.

CONDITIONS EXPERIMENTALES

Le calorimètre adiabatique qui nous a servi à déterminer les transitions de phase de l'AN a déjà été décrit.[7]

Les cellules d'irradiation étaient dégazées et scellées sous une pression résiduelle d'air de 1 à 2×10^{-4} mm de Hg. Les échantillons étaient irradiés par un faisceau vertical de rayons X produit par un accélérateur d'électrons réalisé au Laboratoire et fonctionnant ici sous 1600 kv.[8,9] Après irradiation les cellules étaient réchauffées suivant une méthode standard jusqu'à la fusion du monomère, puis le polymère était séparé du monomère, par évaporation de celui-ci.

Le cryostat utilisé (Fig. 1*a*) est constitué par un four immergé dans l'azote liquide dont la résistance est alimentée à travers un relais de régulation à action proportionnelle et intégrale (construit par MECI, type DAT 1076964) (Fig. 1*b*).

Les spectres RPE ont été obtenus à l'aide d'un spectrographe construit au Laboratoire[10] et fonctionnant à la fréquence de 7000 Mhz/sec. Un dispositif déjà décrit permet de faire des mesures entre —190°C et 20°C.[11] Pour les expériences de RPE, nous avons utilisé des ampoules en quartz Spectrosil de 40 mm de longueur et de 3 à 4 mm de diamètre contenant 0,3 cc de monomère. Elles étaient dégazées et scellées sous une pression résiduelle d'air de 1 à 2×10^{-4} mm de mercure.

ETUDE DES TRANSITIONS DE PHASE DE L'ACRYLONITRILE PAR CALORIMETRIE

1. Résultats Expérimentaux

Trois vitesses de refroidissement du calorimètre ont été utilisées. Après avoir atteint la température de —196°C, on a déterminé les chaleurs

spécifiques C_p en mesurant l'augmentation de température de l'échantillon produite par une quantité connue d'énergie électrique.

D'une part, nous avons refroidi très rapidement l'échantillon en le portant de la température ambiante à $-196°C$ en 4 minutes 30 secondes

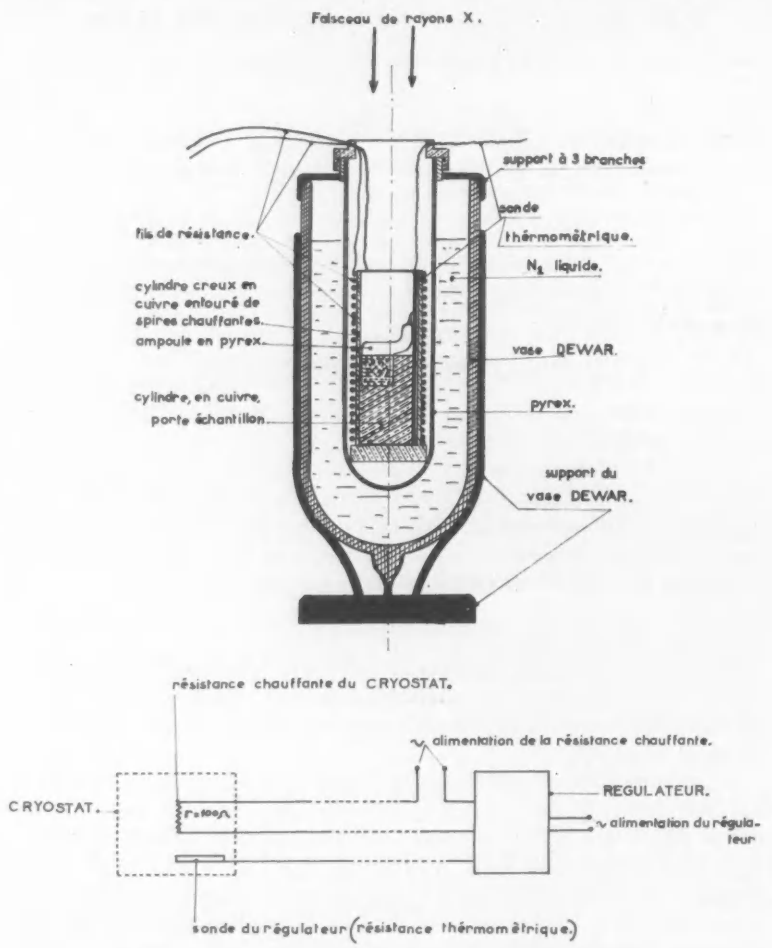


Fig. 1. Schema (*a*) du cryostat; (*b*) des circuits du cryostat.

(50°/min). Au réchauffement, on constate une montée rapide de la chaleur spécifique jusqu'à $-165°C$, puis une chute brusque suivie d'un palier. Vers $-135°C$, un phénomène exothermique spontané dégage 264 cal/mole et on remarque un point de transformation du premier ordre à $-113.1°C$ (Fig. 2*a*).

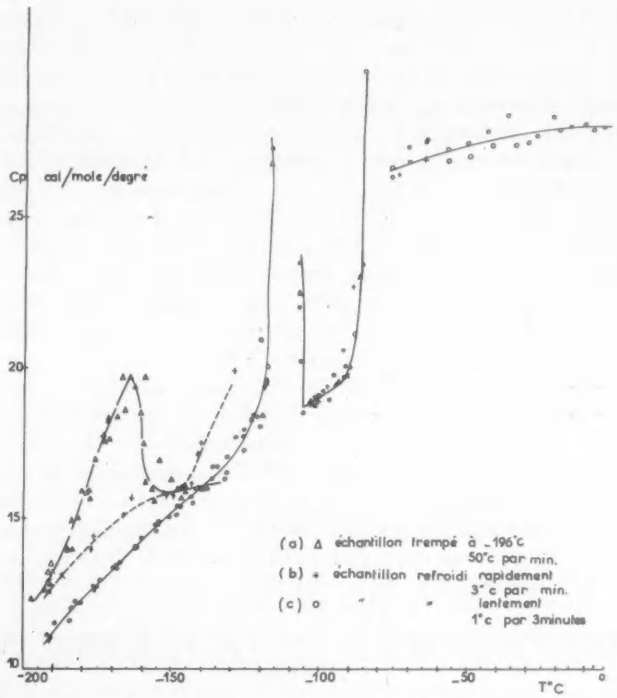


Fig. 2. Variation de la chaleur spécifique de l'AN en fonction de la température.

D'autre part, nous avons refroidi l'échantillon à la vitesse de 3°C par minute. Dans ce cas la chaleur spécifique C_p croît régulièrement entre −196°C et −124°C; à −124°C une élévation spontanée de la température dégage 130 cal/mole puis le comportement de C_p est analogue à celui trouvé dans le 1er cas (Fig. 2*b*).

Enfin, nous avons refroidi lentement l'échantillon (gradient inférieur à 1°C/3 min) de la température ambiante à −196°C en le laissant pendant 2 heures à la température de transition. Dans ce troisième cas, les valeurs de C_p sont inférieures à celles obtenues dans le second cas (Fig. 2*c*).

La chaleur latente de la transition à −113,1°C est de 379 cal/mole. L'acrylonitrile possède donc une forme cristalline basse température (BT) entre −196°C et −113,1°C et une forme cristalline haute température (HT) entre −113,1°C et 83°C. Ces résultats ont déjà été signalés par Magat.[12]

2. Discussion des Particularités de l'Acrylonitrile Mal Cristallisé

Kargin[13] et coll. ont réchauffé de l'acrylonitrile solide condensé à −196°C à partir d'une phase vapeur et constaté par analyse thermique différentielle un dégagement de chaleur à −160°C et à −135°C. Dans ces

conditions le phénomène observé à −160°C serait dû à une transformation verre–cristal. Mais dans notre cas l'aspect du monomère trempé à −196°C, la forme des courbes de chaleur spécifique ainsi qu'une étude préliminaire de diffraction aux rayons X faite par Mr Renaud nous permettent de penser que, par trempe à −196°C de l'AN liquide, nous avons obtenu des cristaux et non pas un verre. Dans notre cas, la variation de C_p pour l'AN refroidi rapidement (Fig. 2, courbes *a* et *b*) s'explique si on admet que la trempe a piégé une partie de l'AN sous sa forme haute température métastable au dessous du point de transition. En effet, au cours du réchauffement, la C_p de l'échantillon trempé présente à −165°C une "bosse": c'est une anomalie de la phase métastable analogue à celles rencontrées dans les phases surrefroidies[14–17] et que nous rapprochons de celles trouvées dans les mélanges de deux composés.[18,19]

A une température plus élevée, il arrive un moment où la rigidité du réseau a suffisamment diminué pour permettre le passage de la forme HT piégée à la forme BT thermodynamiquement stable. Cela se produit exothermiquement à −135°C ou à −125°C selon la vitesse de refroidissement, laquelle a réglé la proportion de la phase piégée. Le rapport de la quantité de chaleur dégagée à la chaleur latente de transformation permet d'évaluer le pourcentage de la phase HT piégée: 70–80% après une trempe, environ 35% après un refroidissement rapide.

RADIOPOLYMERISATION ET POSTPOLYMERISATION DE L'AN SOLIDE

Les résultats précédents nous ont conduits à mettre au point un traitement thermique de recuit conduisant à la forme BT pure. Nous avons ensuite étudié le rendement en polymère en fonction de la température d'irradiation pour les deux formes cristallines du monomère. La méthode utilisée pour mesurer ce rendement (cf. conditions expérimentales) ne nous permet pas de distinguer le polymère formé sous irradiation, du polymère formé pendant le réchauffement.

Nous avons cependant essayé d'évaluer le rendement du post effet dans le cas d'une irradiation à −196°C. C'est pourquoi nous exposerons d'abord les résultats obtenus pour une irradiation à −196°C, puis ceux qui concernent les autres températures.

1. Traitement Thermique Conduisant à une Phase BT Pure

Nous avons trempé les échantillons à −196°C dans l'azote liquide puis nous les avons portés dans notre cryostat à −120°C, température comprise entre la température de recristallisation de la phase HT piégée et la température de transition de phase.

Le rendement en polymère formé par irradiation à −196°C diminue quand le temps de recuit augmente (Fig. 3), c'est-à-dire quand la fraction de phase BT présente augmente. Ce rendement reste constant au-delà de 30 min de recuit, c'est pourquoi nous avons adopté par la suite un mode de

préparation standard comportant une trempe à −196°C suivie d'un recuit de 40 min à −120°C.

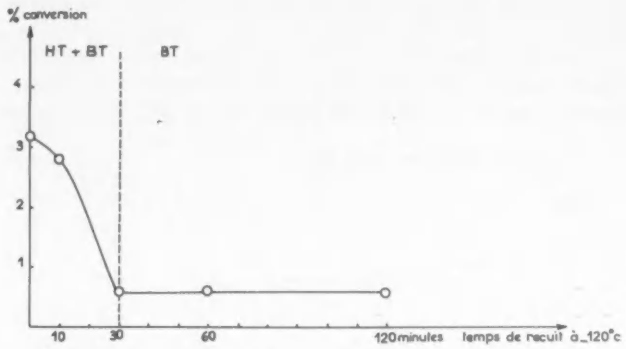


Fig. 3. Rendement en polymère en fonction du temps de recuit.

2. Irradiations a −196°C: Analyse du Post-Effect

Nous avons procédé à quatre types d'analyses après irradiation à −196°C. L'une, calorimétrique, nous a permis d étudier la chaleur dégagée par la réaction de post-effet, la seconde est une analyse thermique différentielle d'un réchauffement rapide, la troisième repose sur une évaluation du rendement en polymère en fonction du traitement thermique des échantillons après leur irradiation, la quatrième a permis de déterminer par RPE l'évolution de la concentration en radicaux au cours du réchauffement.

a. Analyse Calorimetrique. Après une irradiation à −196°C d'un échantillon "recuit" au cours de laquelle l'énergie de rayonnement absorbée correspondait à 135 cal/mole, la réaction de post effet a dégagé en 3 h 20 min de réchauffement 596 cal/mole réparties en fonction de la temperature suivant le diagramme de la Figure 4. Le post effet se manifeste dès −150°C, mais il est plus important autour de la température de transition.

b. Analyse Thermique. Nous avons étudié à l'aide d'un thermocouple et d'un potentiomètre enregistreur un réchauffement rapide analogue à celui effectué au cours de nos expériences de gravimétrie. La comparaison des courbes de réchauffement avant et après irradiation indique qu'une réaction exothermique a lieu aux environs de la température de transition (Fig. 5). On constate que, même pour des temps de réchauffement 20 fois plus courts que ceux de notre expérience de calorimétrie, la réaction de post effet n'est pas négligeable.

c. Postpolymérisation Suivie par Gravimétrie. Nous avons étudié la postpolymérisation de l'AN irradié à −196°C dans sa forme BT (échantillons "recuits") et dans sa forme HT piégée (échantillons "trempés").

Après irradiation, les cellules étaient portées dans un cryostat à une température T pendant des temps variables, puis rechauffées rapidement

dans des conditions standard jusqu'à la température de fusion du monomère.

Nous avons porté les taux de conversion obtenus pour différentes températures T en fonction des temps t de post effet dans le cas d'irradiations d'échantillons "recuits" (Fig. 6) et "trempés" (Fig. 7).

Dans le cas des échantillons recuits, le taux de conversion ne varie pas avec la durée du post effet pour des températures comprises entre $-196°C$ et la température de transition de phase BT → HT, soit vers $-113°C$;

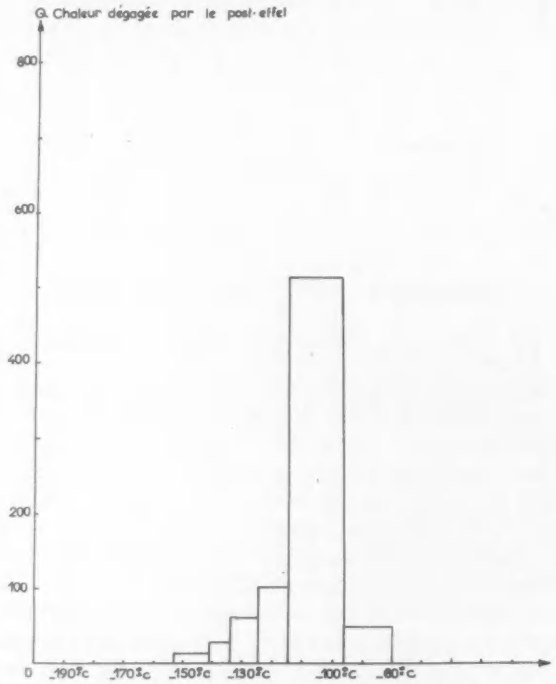


Fig. 4. Analyse calorimétrique du post-effet.

puis il augmente rapidement avec la température et avec le temps jusqu'à la température de fusion (Fig. 6).

Dans le cas des échantillons trempés, la discontinuité de rendement a lieu dès la température de recristallisation de la phase HT → BT, soit vers $-130°C$ (Fig. 7).

Amagi et Chapiro[20] ont obtenu des résultats semblables pour des post-effets d'échantillons trempés étudiés à $-196°C$, $-140°C$, $-115°C$ et $-96°C$.

Si on suppose comme Barkalov[21] que la conversion de post-polymérisation à une température T est une fonction linéaire du temps, le taux de conversion du post-effet ne serait qu'une très faible fraction du taux de

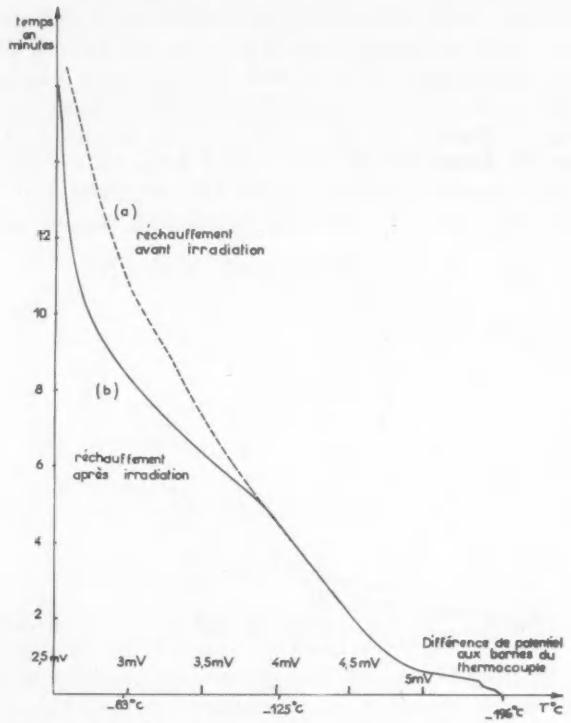


Fig. 5. Analyse thermique du post-effet. Thermocouple cuivre–constantan (jonction de référence à 0°C).

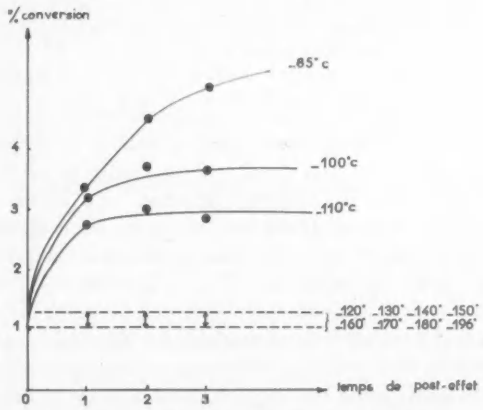


Fig. 6. Post-polymérisation d'échantillons irradiés à −196°C dans la forme BT stable (AN "recuit"). Taux de conversion apres 1 h d'irradiation à −196°C ($7{,}2 \times 10^{19}$ ev/g) suivie de post-effet à différentes températures.

conversion total. Mais nos résultats nous permettent de dire que la variation du rendement en polymère avec le temps ne suit pas une loi linéaire, mais plutôt logarithmique (Fig. 6), c'est pourquoi nous pensons que les vitesses initiales du post-effet sont très grandes et que la post-polymérisation n'est pas négligeable par rapport à la réaction sous irradiation.

d. Etude du Réchauffement par Analyse RPE. Apres irradiation à $-196°C$, on observe[6] un spectre à cinq bandes provenant pour l'essentiel du radical $CH_3—\dot{C}H—CN$, avec une contribution possible de radicaux

$$CH_2=\dot{C}—CN \text{ et } R—CH_2—\dot{C}H—CN.$$

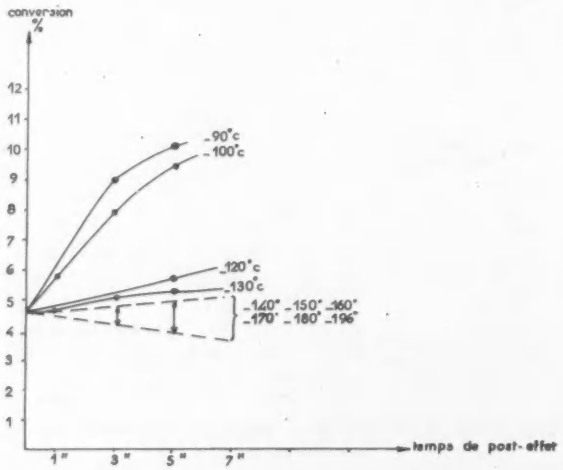


Fig. 7. Post-polymérisation d'échantillons irradiés à $-196°C$ dans la forme HT piégée (AN "trempé"). Taux de conversion apres 1 h d'irradiation à $-196°C$ ($10{,}8 \times 10^{19}$ ev/g) suivie de post-effet à différentes températures.

Dans les échantillons trempés, la variation de la concentration des radicaux au cours du réchauffement fait apparaître l'existence de quatre domaines de température. La courbe de la Figure 8*a* correspond à une vitesse de chauffe de 1,5°C/minute environ. La forme des spectres (caractérisée par le rapport d'intensité de la bande centrale à la bande contigüe) varie de façon continue dans le domaine II pour aboutir au spectre à trois bandes du radical $R—CH_2—\dot{C}H—CN$.

Dans le domaine I, l'augmentation apparente du nombre de radicaux est probablement due à un effet de saturation de puissance, variable avec la température.[22]

Dans le domaine II, où a lieu la recristallisation de la phase HT piégée en phase BT stable, on observe une recombinaison rapide des radicaux.

Dans le domaine III, où nous avons la phase BT stable, la vitesse de recombinaison diminue considérablement.

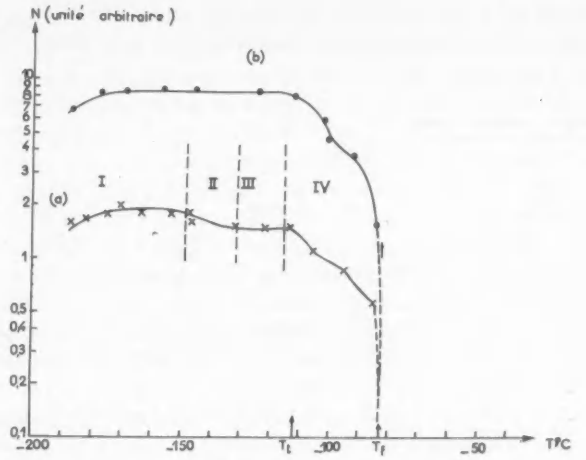


Fig. 8. Variation du nombre de radicaux au cours du réchauffement d'un échantillon irradié à −196°C: (●) échantillon recuit; (×) échantillon trempé.

Et enfin, dans le domaine IV, qui englobe (*a*) la transition BT → HT, (*b*) la phase HT, (*c*) la préfusion, on observe une recombinaison des radicaux, plus rapide dans (*a*) et (*c*) que dans (*b*).

Pour les échantillons recuits, les domaines I, II et III sont confondus (Fig. 8*b*), et la concentration des radicaux reste constante jusqu'à −115°C.

Le domaine IV peut être décomposé, dans ce cas avec plus de certitude que dans l'experience precedente, en trois parties: une vitesse de recombinaison élevée entre −120 et −105°C (transition BT → HT), lente entre −105 et −90°C (phase HT stable), rapide entre −90°C et la température de fusion (domaine de préfusion). La transformation des spectres se produit entre −120° et −110°C.

Le rendement en radicaux mesuré à −196°C est indépendant du traitement thermique subi par les échantillons avant irradiation. La valeur moyenne déterminée entre 10^{20} et 5×10^{20} eV/g est de $G_{R_1} = (0{,}6 \pm 0.1)$.

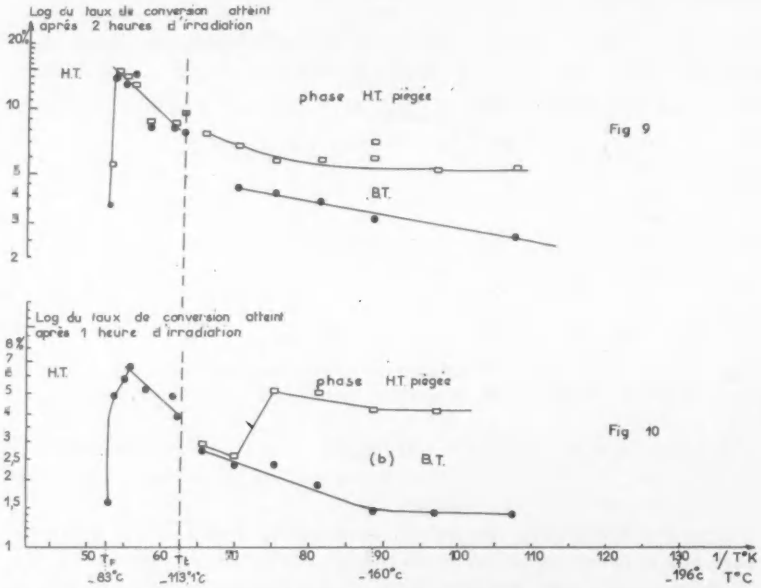
3. Résultats de l'Irradiation aux Autres Températures

Les débits de dose étaient de 12.500 rads/min et tous les traitements thermiques commençaient par une trempe à −196°C quelle que soit la température d'irradiation. La phase BT pure a été préparée suivant le traitement thermique de recuit décrit plus haut. Nous rappellerons que la fraction de la phase HT piégée dans les échantillons trempés dans l'azote liquide peut être évaluée à environ 80% d'après notre étude calorimétrique.

Entre −196°C et $T_t = -113{,}1$°C, le rendement total en polymère de la phase BT pure est inférieure au rendement de la phase HT piégée (Fig. 9).

Par ailleurs, si on maintient l'échantillon trempé 50 à 60 minutes à la température d'irradiation avant d'irradier, le rendement diminue brusque-

ment à partir de −140°C jusqu'à la température de transition (Fig. 10*a*) ce qui indique qu'une recristallisation conduisant à la phase BT stable commence à partir de −140°C.



Figs. 9 et 10. Log taux de conversion en fonction de l'inverse de la température: (●) échantillons trempés à −196°C, recuits à −120°C puis portés à la température de l'irradiation; (□) échantillons trempés à −196°C puis portés à la températuredel'irradiation.

Si on irradie la phase HT piégée dès qu'elle a atteint la température d'irradiation cette recristallisation n'a pas encore lieu même au bout de 120 min (Fig. 9). Il est probable que la présence de polymère qui se forme dans la phase HT piégée ralentit la transformation de la phase métastable. D'une manière un peu analogue, des études d'absorption dipolaire Debye ont montré que l'addition d'un composé favorisait le maintien de l'état surrefroidi.[23]

Entre −113,1°C et −83°C, le rendement en polymère est à peu près le même, que les échantillons aient subi ou non un recuit. D'autre part, le rendement augmente rapidement avec la température. A −84°C, température proche de la température de fusion, le rendement baisse brusquement (Figs. 9 et 10).

4. Discussion

a. Réaction sous Irradiation et Réaction de Post-Effet. Un des problèmes les plus importants des réactions radiochimiques en phase solide est

la détermination exacte de la part du post-effet dans le rendement total. La cinétique du post-effet à chaque température ne peut nous donner qu'une réponse approximative car le taux de conversion du post-effet est une fonction logarithmique du temps et les vitesses initiales sont, dans ce cas, difficiles à évaluer avec précision.

La calorimétrie effectuée au cours de l'irradiation et après l'irradiation pourra répondre plus précisément à la question posée.

Un second problème reste à résoudre: les résultats de radiopolymérisation montrent qu'une réaction dont le rendement augmente avec la température a lieu dans la phase BT pure, sous irradiation alors qu'il n'y a pas de post-effet dans cette phase; d'autre part les études de RPE ont montré la présence après irradiation de radicaux CH_3—$\dot{C}H$—CN à −190°C, qui n'ont pas amorcé de polymérisation sous irradiation dans la phase BT et qui en amorceront une au cours du réchauffement à partir de la température de transition. On est alors conduit, pour expliquer ces faits, à admettre l'existence de deux types de centres actifs d'après l'hypothèse suivante.

Des centres actifs primaires C* possèdent à leur naissance une énergie E, électronique, vibrationnelle et rotationnelle supérieure à celle des centres dont nous observons les réactions au cours du réchauffement. Cette énergie peut leur premettre d'amorcer une réaction exothermique de propagation:

$$C^* + M \rightarrow CM^* \qquad (1)$$

qui dégage une énergie Q. Les pertes d'énergie par collision étant réduites puisque nous sommes en phase solide, CM* disposera de la chaleur de la réaction (1) et, comme le suppose Magat[24] à partir d'une suggestion de Semenov[25] basée sur la théorie des chaînes énergétiques de Christiansen, une nouvelle addition se produira:

$$CM^* + M \rightarrow CM_2^* \qquad (2)$$

et ainsi de suite.

Les centres actifs C qui n'ont pas eu d'energie suffisante pour la réaction (1) ou qui n'en ont plus assez pour que la chaîne se propage, sont alors responsables du post-effet observé au cours du rechauffement à partir de la température de transition de phase. La vitesse de post-effet diminue au fur et à mesure que la polymérisation progresse: on peut penser que la propagation détruit le cristal et diminue la probabilité de présence des molécules de monomère favorablement orientées dans la proximité de le chaine croissante.

b. Comparaison des Rendements Obtenus par Irradiation des Formes HT et BT. Les expériences de RPE indiquent qu'à −196°C, le rendement en radicaux est le même que les échantillons aient été irradiés dans la forme BT ou la forme HT métastable. Comme nous pensons que la polymérisation est radicalaire,[6] la différence du rendement en polymère entre la forme BT stable et la forme HT métastable provient d'une différence de vitesse de propagation, et pourrait être due au fait que la phase HT piégée présente

une liberté de mouvement plus grande que la phase BT stable, ce qui augmente la probabilité d'une orientation favorable à la propagation. Nous ne pensons pas que la différence de rendement puisse être due uniquement à une orientation favorable fixe, de la molécule de monomère dans la maille cristalline de la phase HT et cela pour deux raisons: la première est que les résultats de post polymérisation montrent que la réaction a surtout lieu à la transition de phase au moment où les molécules ont une certaine liberté, la seconde est que certaines polymérisations en phase vitreuse ont un rendement plus élevé qu'en phase cristalline, c'est le cas, par exemple, de l'acétate de vinyle,[21] du *N*-vinylcaprolactame,[26] du méthacrylate de méthyle dans l'huile de paraffine.[20]

c. Variation du Rendement avec la Température. L'hypothèse que les mouvements moléculaires favorisent la réaction expliquerait aussi la variation du rendement en fonction de la température. En effet, l'augmentation de température entre −196°C et −113,1°C modifie peu les caractéristiques du cristal car il est probable que seules les vibrations sont affectées (c'est le cas de nombreux cristaux moléculaires[27] au-dessous de la température de transition) et le rendement varie peu; par contre, dans la phase HT des rotations ou des librations apparaissent, leur vitesse et leur amplitude augmentent avec la température et introduisent la discontinuité observée dans le rendement à partir de −113,1°C.

Les courbes de C_p montrent une discontinuité à −90°C probablement due à l'apparition de mouvements moléculaires de translation. Ces mouvements facilitent la recombinaison des centres actifs et expliquent la chute du rendement à −84°C. Il est probable que si la transition de phase solide BT → HT à −113,1°C n'introduit pas une disparition des centres actifs aussi rapide, cela tient au fait que les mouvements moléculaires sont plus limités qu'à la préfusion: la variation d'entropie est $\Delta S_{\text{trans.}} = 2.36$ cal/mole/degré alors que $\Delta S_{\text{fus.}} = 8.15$ cal/mole/degré. Des études de résonance magnétique nucléaire et de cristallographie sur l'acrylonitrile solide sont en cours; elles préciseront le rôle des mouvements moléculaires et des structures de ce monomère dans la cinétique de la réaction.

CONCLUSION

Certains travaux ont montré que la structure cristalline d'un monomère était un facteur essentiel des réactions en phase solide qui le mettent en jeu; c'est surtout le cas des radiopolymérisations de l'acétaldéhyde,[28] du trioxane,[29] du dicetene[29] (où la chaîne du polymère est préfigurée dans le cristal), de la radiopolymérisation des sels des acides acryliques et méthacryliques[30] ou de la dimérisation photochimique de l'acide transcinnamique.[31]

Notre étude montre en outre l'existence de discontinuités cinétiques aux points de transition de phase et souligne un second facteur qui peut être important dans les réactions en phase solide: la nécessité d'une certaine liberté de mouvement des molécules. Celle-ci permet de comprendre que les défauts et les dislocations où les mouvements moléculaires sont plus

libres, sont des régions favorables aux polymérisations en phase solide[32,33] et d'expliquer que certaines polymérisations aient un rendement plus élevé en milieu vitreux qu'en milieu cristallin.[20,21,26]

Nos résultats sont à rapprocher des observations sur la disparition des radicaux libres au voisinage des points de transition de phase dans les cristaux moléculaires[34–37] et sur la réactivité chimique anormale de certains composés minéraux, observée par Hedvall[38] au voisinage des points de transition.

Nous tenons à remercier pour leur collaboration Monsieur Leonardi et toute l'équipe de l'accélérateur d'électrons du laboratoire, en particulier Messieurs Boivin, B. Fourmann, R. Peltier, et P. Pernot.

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Résumé

Une étude de la chaleur spécifique de l'acrylonitrile solide entre −196°C et −83°C. solidifié suivant différentes méthodes, nous a conduit à examiner le rôle des conditions de cristallisation et des transitions de phase sur le rendement en polymère et le dégagement de chaleur obtenus après irradiation de ce monomère en phase solide. Nous avons constaté que les transitions de phase expliquent nos résultats cinétiques et calorimétriques.

Synopsis

The specific heat of solid acrylonitrile has been studied between −196 and −83°C after solidification with different methods. The influence of the crystallization and of the phase transition conditions on the yield of polymer and the heat evolution after irradiation of this monomer in solid state have been examined. It is shown that phase transitions explain the kinetic and calorimetric results.

Zusammenfassung

Eine Untersuchung der spezifischen Wärme des nach verschiedenen Methoden in den festen Zustand überführten festen Acrylnitrils hat uns zu einer Überprüfung der Rolle der Kristallisations- und Phasenumwandlungsbedingungen für die Polymerausbeute und die nach Bestrahlung dieses Monomeren in fester Phase erhaltene Wärmeentwicklung veranlasst. Es wurde festgestellt, die kinetischen und kalorimetrischen Ergebnisse durch die Kristallumwandlungen und die Kristalldimensionen erklärt werden können.

Discussion

Y. Tabata (*Tokyo, Japan*): I would like to comment about the polymerization of acrylonitrile. As reported before, we could obtain a high stereoregular polyacrylonitrile from the pure monomer system in the solid-state polymerization at low temperature. Recently, we also could obtain another type of stereoregular polyacrylonitrile from mixed systems of acrylonitrile with propionitrile, alcohols, methacrylonitrile, and several other organic compounds. We observed marked differences between the infrared spectra of these polymers and also found obvious differences between the x-ray diffraction curves of the heat-treated specimens. Now, we believe from our experimental results, that the structure of the polymer which was obtained from the pure monomer system is syndiotactic and that the mixed systems lead to a planar zig-zag type isotactic structure.

R. Bensasson: The synthesis of syndiotactic or isotactic polyamylonitrile has always failed. Hence the results of Dr. Tabata are very interesting. The various methods of synthesis used in the liquid state have always given the same type of structure. Such methods as polymerization at low temperatures which leads to stereoregularity in polyvinylchloride (G. Natta, et al., *J. Polymer Sci.*, **20,** 251 (1956)) and in polymethylmethacrylate (Fox et al., *J. Ac.*, **80,** 1768 (1958)) and the use of organometallic initiators which also yields a stereoregular polymethylmethacrylate (Fox et al., *J. Ac.*, **80,** 1768 (1958)) and many stereoregular hydrocarbon, gave a polyacrylonitrile identical with that prepared by conventional free radical initiator (Bohn et al., *J. Polymer Sci.*, **55,** 531 (1961)) which is atactic and paracrystalline (Lindenmeyer H. et al., *J. Appl. Phys.*, **34,** 42 (1963)).

However our preliminary IR and X diffraction studies of polyacrylonitrile structure have not shown marked differences between the polymers prepared by irradiation of the liquid monomers at 20°C. and those prepared by irradiation of the solid monomers at −196°C. or −100°C.

H. Morawetz (*Polytechnic Institute, Brooklyn, N. Y.*): The calorimetric technique employed by the authors has the great virtue that artifacts which may be produced when polymer is separated from residual monomer are avoided. It is to be desired that more techniques with this characteristic will be used in solid-state polymerization studies. In the paper with Jakabhazy presented to this symposium we show how useful IR spectroscopy can be in this context. If single polymerizing crystals are used, investigations of infrared dichroism, ESR spectroscopy and x-ray crystallography may go far to define the extent to which the geometrical ordering of the monomer crystal affects the polymerization process.

R. Bensasson: Nous sommes tout à fait d'accord avec les remarques générales du Dr. Morawetz sur la necessité d'études physiques sur les monomères solides. Nous nous proposons d'ailleurs de verifier notre hypothèse sur le rôle des mouvements moléculaires dans la polymérisation de l'acrylonitrile par des études de cristallographie et de résonance magnetique nucléaire à differentes températures.

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Radiation-Induced Solid-Phase Polymerization. I. Polymerization of Acrylonitrile

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I. INTRODUCTION

Mesrobian et al.[1] reported in 1954 on the radiation-induced polymerization of solid acrylamide. A great amount of experimental work has been published in subsequent years. It was shown that the radiation-induced solid-phase polymerization proceeds at a considerable rate,[2–4] and at present this problem appears to be of great interest both for practical applications and for the development of general chemical kinetics concepts.

The routine method for investigating the kinetics of radiation-induced solid-phase polymerization involves irradiation of the solid monomer with subsequent heating (up to the melting point), separation of the monomer from the polymer, and determination of the polymer yield. Thus the polymer yield and the polymerization rate are determined after irradiation and subsequent strong heating accompanied with melting, and often also with phase transitions (before melting). As a result of this the data obtained appear to be very vague, as these do not show whether polymerization of the given monomer proceeds in the solid phase (and how, i.e., in the course of irradiation or by post-effects), or in the heating up, for example at phase transition points, as shown by Kargin et al.,[5,6] or at the melting point.[7–9] Yet, to establish the mechanism of polymerization it is very important to know when polymerization occurs.

A detailed investigation of the radiation-induced solid-phase polymerization of a number of monomers was undertaken in this connection. It involved the study of initial polymerization rate as a function of temperature, calorimetric measurements of liberation (or absorption) of heat in the heating up of irradiated monomers, observation of ESR signals (during and after irradiation), determination of the kinetics of post-polymerization, and measurement of molecular weights of the polymers studied. The radiation-induced polymerization of acrylonitrile (AN), CH_2=CH—CN, m.p. −82°C., b.p. +78.5°C., was studied first. The effective development of this process in the solid phase was demonstrated by Bensasson and Marx,[10] Sobue and Tabata,[11] and especially by Amagi,[12] who studied also the solid-phase post-polymerization. Nevertheless a

considerable amount of information that can be used for the elucidation of the polymerization mechanism was first obtained in the given work.

A second communcation[13] is concerned with radiation-induced solid-phase polymerization of vinyl acetate and with the temperature dependence of the initial polymerization rate for a number of other monomers; certain conclusions will be given.

II. EXPERIMENTAL

The polymerization of acrylonitrile over the range of −196 to 0°C. was initiated by 1.6 w.e.v. electrons from an accelerator designed at the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences. The monomer, dried and distilled in a rectification column, was freed from air in vacuum and frozen into special cells for irradiation.[14] An automatic holder (for 8 cells) permitting remote control in the course of irradiation (without interrupting the irradiation) was used. The holder was placed in a foam plastic bath thermostatted with an accuracy to within ±0.5°C. over a temperature range of −30 to −196°C. with nitrogen vapor that was admitted through an adjustable heater. An alcohol thermostat with the same accuracy of thermostatting was used for higher temperatures (−30 to 0°C.). In order to minimize the post-effect, the cells were rapidly heated to room temperature after irradiation. An inhibitor solution (hydroquinone) was added during the heating up in the first experiments, but as it did not change the yield, it was not added in later runs. The polymer yield was determined after drying of the monomer sample in vacuum to a constant weight. The relative radiation dose was determined from the electron current by means of a thin film placed in front of the cell. Absolute dosimetry was carried out by means of an ionization chamber and a ferrosulfate dosimeter.[15] The dose intensity for various experiments was in the range of 0.2–2 Mrad/min.

In order to determine whether the polymerization is more effective during the solid-phase irradiation or during the heating up, a diathermic calorimeter was designed on the basis of a principle suggested by Kapustinskiĭ and Barskiĭ.[16] The calorimeter design permitted irradiation of the monomer directly in the calorimetric cell. The sample temperature and the difference in temperatures of the external and internal sides of the diathermic envelope, proportional to the heat flow, were measured simultaneously during the heating of the sample by use of a battery of differential thermocouples and a highly sensitive recording potentiometer. Heats of 10–40 cal./g. were measured with an accuracy to within ±1 cal./g.

The kinetics of accumulation of active centers in the course of AN irradiation at various temperatures was studied by using the ESR technique. This work was done in conjunction with Shamshev, whose help is sincerely acknowledged. The apparatus used has been described by Molin et al.[17]

To study post-polymerization kinetics the samples were kept for a certain time after irradiation in a cryostat which maintained the required

temperature to ±2°C., and then were subjected to rapid heating, after which the polymer yield was determined. The intrinsic viscosity (in dimethylformamide solution) of each polymer sample was also determined, and then the molecular weights were calculated by the equation:[18]

$$[\eta] = 2.43 \times 10^{-4}\bar{M}^{0.75}$$

III. RESULTS

The kinetic curves for polymerization of acrylonitrile in the liquid and solid phase are shown in Figure 1. In the liquid phase the polymerization

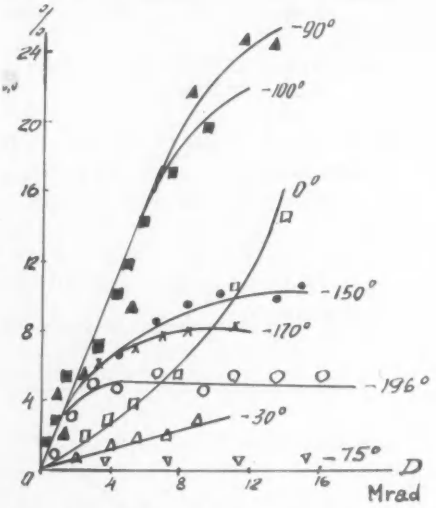

Fig. 1. Kinetic curves for radiation-induced polymerization of AN at various temperatures in the liquid and solid phases (I = 0.75 Mrad/min. and 0.3 Mrad/min., respectively).

rate decreases with temperature, and close to the melting point (−75°C.) it becomes practically zero. At the same time a very high reaction rate is observed for the solid phase close to the melting point (−90°C.). It may be seen from Figure 1 that the kinetic curves for acrylonitrile polymerization in the solid phase at −196 and −170°C. (and less so at −150°C.) tend to a limit increasing with temperature. At higher temperatures this is observed neither for the solid nor for the liquid phase.

The most striking example of a limiting polymer yield is the kinetic curve for −196°C. (Fig. 2). The points on this curve were obtained for a range of dose intensities of 0.30–3.0 Mrad/min. In certain sets of experiments irradiation with a dose corresponding to the limiting yield (8 Mrad) was repeated several times with subsequent heating to room temperature

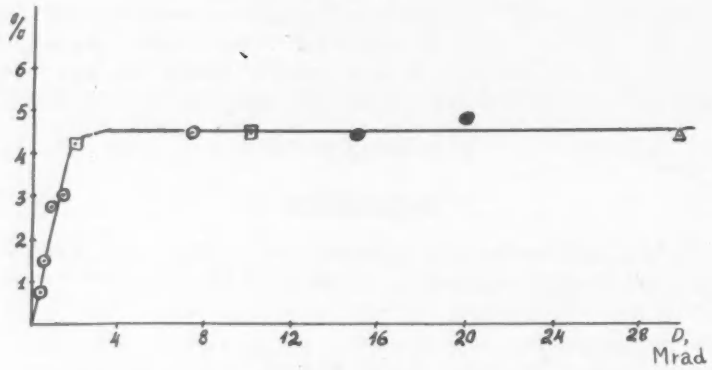

Fig. 2. Kinetic curve for AN polymerization at −196°C.: (⊙) $I = 0.3$ Mrad/min.; (⊡) $I = 0.5$ Mrad/min.; (●) $I = 1.0$ Mrad/min.; (△) $I = 3$ Mrad/min.

and melting, and then freezing to −196°C. Every irradiation increased the polymer yield, the increase being equal to the limiting yield value for a single irradiation (for example 4.6% for one irradiation, 9.3% for two, 12.6% for three irradiations). The initial rate of AN polymerization as a function of the radiation intensity I at −196°C., $V \simeq I^{0.8}$ is shown in Figure 3. A similar function is observed for radiation-induced polymerization of AN in the liquid phase.[19]

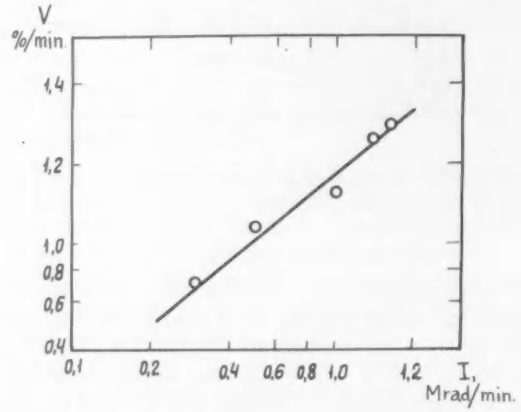

Fig. 3. The initial rate of AN polymerization as a function of radiation intensity (at −196°C.).

The temperature dependence of the initial AN polymerization rate is shown in Figure 4 and appears to give an activation energy $E \simeq 3$ kcal./mole of the liquid. E is close to zero for the solid phase. Determinations of the molecular weight of polyacrylonitrile for all temperatures studied

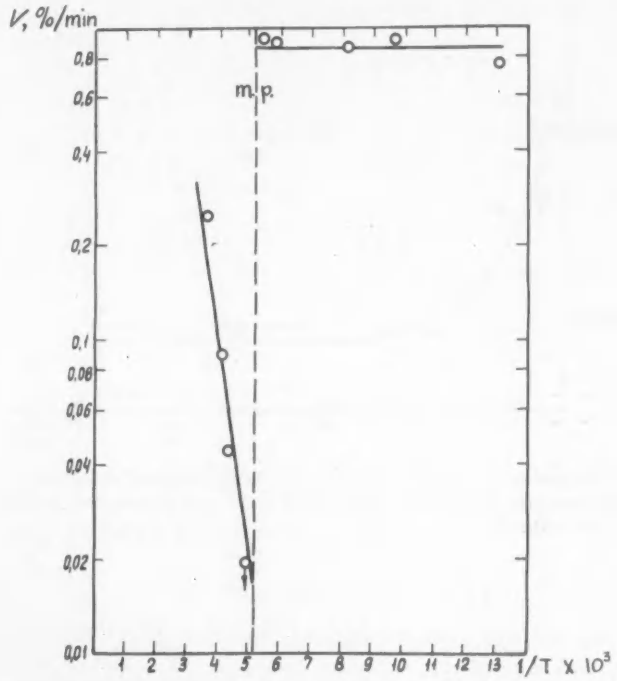

Fig. 4. The temperature dependence of the initial AN polymerization rate.

show a systematic decrease in $\bar{M}$ with increasing doses, tending to a certain limit. The $\bar{M}$ values are independent of the radiation intensity (Fig. 5).

Solid-phase post-polymerization was found to occur at −140, −120, and −90°C., and to be absent at −196°C. (as well as at other temperatures below −140°C.[12] The kinetic curve for post-polymerization at −90°C. at a radiation dose of 2.5 Mrad is shown in Figure 6, which illustrates also the absence of post-polymerization at −196°C. The activation energy for solid-phase post-polymerization was 3 kcal./mole (in agreement with the data of Amagi[12]), i.e., the same as for the liquid-phase radiation-induced polymerization.

A great increase in the molecular weight of the polymer was observed in the course of post-polymerization; irradiation with a dose of 2 Mrad at −196°C. gave $\bar{M} \simeq 2 \times 10^5$, and after post-polymerization for 10 hr. at −90°C. the value was $\bar{M} \approx 10^6$. After the lapse of a still longer time the polymer became insoluble in dimethylformamide, i.e., a crosslinked polymer was formed.

The ESR signals from solid AN both during the course of irradiation and after it were found to be similar. The kinetic curves for active centers

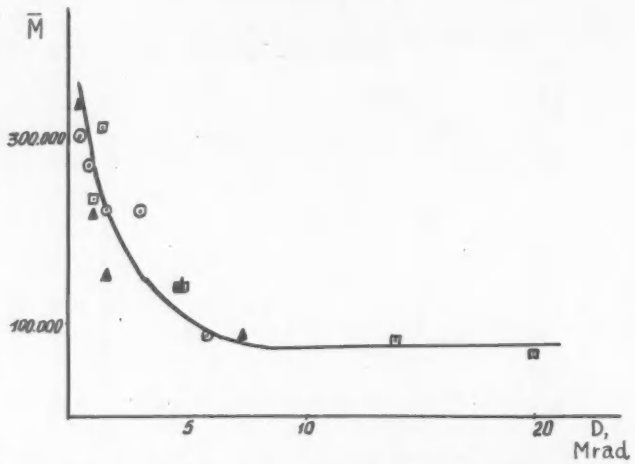

Fig. 5. The molecular weight of polyacrylonitrile as a function of the dose at various radiation intensities: (⊙) I = 0.3 Mrad/min.; (△) I = 1.0 Mrad/min.; (⊡) I = 3.0 Mrad/min. at −196°C.

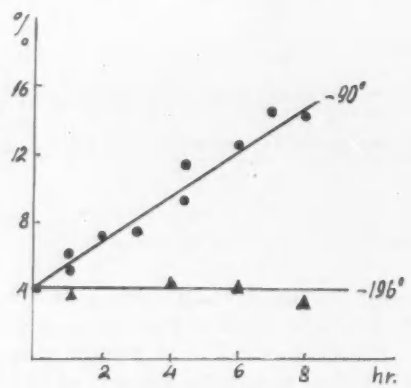

Fig. 6. Kinetic curves for AN post-polymerization (initial samples irradiated with D = 2.5 Mrad at I = 0.5 Mrad/min.

showing ESR signals in the course of irradiation are given in Figure 7 for −173, −150, and −120°C. The signal intensity did not decrease after irradiation, when the sample was kept at −172°C. for 30 minutes.

Calorimetric measurements show that the heat of melting of AN is 35 ± cal./g. As the heat of polymerization of this monomer is 327 cal./g.,[20] the formation of 1% of the polymer at the melting point should have lowered the heat of melting by some 9%. However, no such change (within the experimental error mentioned, i.e., ±1 cal./g.) was observed for AN samples irradiated at low temperatures with a 12% polymer yield

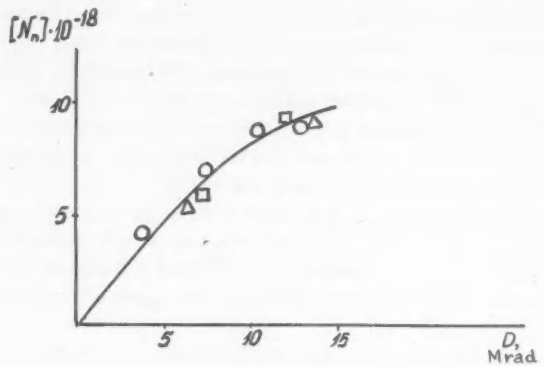

Fig. 7. Kinetic curve for the accumulation of active centers in the irradiation of solid AN (I = 0.3 Mrad/min.): (⊙) −120°C., (△) −150°C., (□) −173°C.

(temperature of irradiation −100°C., D = 8 Mrad). It may be seen from post-polymerization rates (Fig. 6) that no appreciable polymer formation will occur in the course of fast heating of the samples as well.

IV. DISCUSSION

The main experimental evidence obtained by using the calorimetry technique is that both in the course of irradiation and after it AN polymerization will occur exactly in the solid phase. The mechanism of solid-phase polymerization in the course of irradiation is obviously different from that for post-polymerization. This may be seen, for instance, from the difference in activation energies for the two cases.

The solid-phase polymerization rate in the course of irradiation is considerably higher than that obtained by extrapolation of the values for liquid-phase polymerization. For instance, in passing from the liquid to the solid phase at the same radiation dose the polymerization rate increases by more than a power of ten (and as the polymerization rate dependence on $V_0 \sim I^{0.8}$ is similar both for the solid and the liquid phase, for AN this increase will be of an absolute nature and independent of I).

The rate of solid-phase polymerization in the course of irradiation is very different from the post-polymerization rate as well. It was mentioned before that at a temperature of −140°C. no post-polymerization of AN occurs. At a temperature of −90°C., for example, a 12% conversion by post-polymerization would take 9 hr., while in the course of irradiation, at I = 0.3 Mrad/min. it takes only 15 min. It was already mentioned that the activation energies for liquid-phase radiation-induced polymerization and for solid-state post-polymerization are close. Therefore it may be concluded that the nature of active centers and the mechanism of chain propagation for liquid-phase polymerization in the course of irradiation and for solid-phase post-polymerization also will be similar. It

will be of interest to note that the post-effect disappears at a temperature lower than that of the phase transition reported by Amagi[12] (−140°C.). The existence of a definite limiting polymer yield value for the polymerization during irradiation is observed also only below −140°C.

The mechanism of solid-phase polymerization in the course of irradiation is specific and essentially different from the processes discussed above. It is most pronounced at temperatures below −140°C., when there is no post-effect. A polymerization of this kind will be terminated immediately after the radiation is cut off, in spite of the persisting shape and intensity of the ESR signal and of the long lifetimes of ions in solids at low temperatures. Thus the specific polymerization in the course of irradiation cannot be due to radicals and/or ions only. The possible reason for effective solid-phase polymerization in the course of irradiation may be the formation of short-lived excited molecules that would, naturally, decay even in the solid phase after irradiation is cut off, while their steady-state concentrations in the liquid phase would be considerably smaller due to quenching. Active centers of this kind may appear to be considerably more effective than ions or radicals in the development of polymerization by the energy chain mechanism suggested by Semenov[21,22] (see also Adirovich[23]). Another reason for the acceleration of solid-phase radiation-induced polymerization might lie in a change of the solid in the course of irradiation.

Local heating along tracks accompanied by specific ionization may be of great importance in the irradiation with heavy particles.[24,25] However, for 1.6 m.e.v. electrons such heating would not exceed several degrees (this may be shown from the data of Goldanskiĭ and Kagan[24]) and, consequently, would be of minor importance. The "loosening" of the substance along tracks of primary particles and δ-electrons appears to be considerably more important; this seems to be responsible also for the radiation-induced acceleration of diffusion.[26,27] The possibility of molecular displacements in the solid under the action of electron inpact, of momentary defreezing of internal rotation, and the excitation of various vibrations would make the properties of the irradiated solid similar to those observed close to phase transition or melting points and known to favor effective polymerization.[5,6,21,22]

Now let us attempt to interpret the other facts observed. A simple explanation for the occurrence of solid-phase polymerization without activation energy lies within the scope of Semenov's theory (energy chain, for example of the exciton energy transfer type). However, the possibility of another, more trivial, explanation will be noted. This would be a polymerization mechanism in which the chain length would be a function of certain space conditions, and not of the competing chain termination and chain propagation reactions. In other words, the chain length would be predetermined by the properties of the given substance. Then the expression for radiation-induced polymerization, $V = k_0 I_\nu$, where the only temperature-dependent term usually is the chain length ν, will contain no temperature dependence at all, and E will be zero. However, in this case

the chain propagation time will be a function of the activation energy for every chain link and will be, by order of magnitude, $10^{-13} \exp \{E/RT\}$ sec. At $E = 3$ kcal./mole (the activation energy for AN post-polymerization) and at -196°C. this would give about 10^{-4} sec. The time of growth of the overall AN chain (at $\overline{M} = 10^5$) would then be approximately 0.2 sec. As polymerization at -196°C. will proceed only during the irradiation, pulsed irradiation might be used for final refutation of the suggestion that the absence of activation energy is due to a predetermined chain length. In these experiments the chain length would not exceed 10^{-4}–10^{-3} sec., and the intervals should be considerably longer than the lifetimes of excited states that may be responsible for the growth of polymer chains under irradiation.

The occurrence of a certain limiting value of the polyacrylonitrile yield setting in at temperatures less than -140°C. and increasing with temperature, as well as its increase in proportion to the number of heatings and repeated irradiations may be due to "preorientation" of the future polymer in the solid monomer. After exhaustion of these preorientations further irradiation would lead only to a decreasing molecular weight of the polymer.

V. SUMMARY

The radiation-induced polymerization of acrylonitrile (AN) was investigated over a temperature range of -196 to 0°C., both in the solid and in the liquid phase.

The activation energy for AN polymerization is zero for the solid, and 3 kcal./mole for the liquid phase.

No post-effect is observed for polymerization in the solid phase at -196, -170, and -150°C., and there exists a certain limiting polymer yield at these temperatures for high doses. Repeated high-dose irradiations with melting of the sample in intervals between such irradiations results in an increase in the yield in proportion to the number of irradiations. The molecular weight of the polymer obtained decreases with increasing radiation doses.

The activation energy for post-polymerization is 3 kcal./mole (i.e., similar to that for the liquid phase). The molecular weight of the polymer obtained displays an essential increase in the course of post-polymerization.

Calorimetric measurements show that solid-phase polymerization occurs during irradiation (completely at <-140°C., and almost so, with minor post-effects, at >-140°C.), though the shape and intensity of the ESR signal from the sample persist after irradiation.

The radiation-induced polymerization observed is terminated immediately after radiation is cut off, in spite of the persisting shape and intensity of the ESR signal and of the long lifetimes of ions in solids at low temperatures. Thus the specific polymerization in the course of irradiation cannot be due to radicals and/or ions only. The results obtained are interpreted from the standpoint of specific solid-phase polymerization

during irradiation (for instance, by the energy chain mechanism of Adirovich[23]), favored by the formation of short-lived excited molecular states and by loosening of the substance in the course of irradiation.

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Synopsis

Radiation-induced polymerization of solid and liquid acrylonitrile (AN) at −196 to 0°C. was studied. A diathermic calorimeter was used to determine whether polymerization takes place in the solid state during irradiation or during the subsequent heating. The presence of active centers during irradiation of AN at different temperatures and their disappearance after irradiation was detected by the ESR method. Post-polymerization kinetics was studied as well. In AN at <-140°C. (phase-transition point), solid-state polymerization takes place only during irradiation. There is a certain limiting polymer yield, and no post-effects are observed in spite of persistence of the shape and intensity of the ESR signal after the end of irradiation. The activation energy of solid-state polymerization of AN is zero up to the melting point (−82°C.). At temperatures greater than −140°C., the AN polymer yield in the solid state is no longer limited, and post-polymerization takes place, its activation energy (~3 kcal./mole) being the same as for the polymerization in the liquid phase. Thus, the solid-state post-polymerization mechanism is similar to that of the liquid-state process, and differs from that of the solid-state polymerization during irradiation. These facts are evidence for specificity of radiation-induced solid-state polymerization during irradiation. The high efficiency of such polymerization is probably caused by the formation of short-lived excited molecular states. Such states decay soon after the end of the solid-state irradiation (although the ESR signal persists) and for the liquid phase their steady-state concentrations during the irradiation are much less due to increase in the quenching rate. Such active centers can be much more effective than ions or radicals in the energy-chain propagation of solid-state polymerization as suggested by Semenov.

Résumé

On a étudié la polymérisation de l'acrylonitrile (AN) induite par radiation entre −196° et 0°C. On a utilisé un calorimètre diathermique en vue de déterminer si la polymérisation a lieu dans l'état solide au cours de l'irradiation ou au cours du chauffage subséquent. On a détecté la présence de centres actifs au cours de l'irradiation de l'AN à différentes températures et leur disparation après irradiation au moyen de la méthode de RSE. On a aussi étudié la cinétique de post-polymérisation. Dans l'AN à moins de −140°C (point de transition de phase) la polymérisation en phase solide n'a lieu qu'au cours de l'irradiation. Il y a un certain rendement limitatif en polymère et on n'observe aucun effet postérieur en dépit de la persistance de forme et d intensité du signal RSE après la fin de l'irradiation. L'énergie d'activation de la polymérisation à l'état solide de l'AN est nulle jusqu'au point de fusion (−82°C) aux températures supérieures à −140°C, le rendement en polymère AN dans la phase solide n'est plus limité et une post-polymérisation a lieu; son énergie d'activation était égale à celle de la polymérisation en phase liquide (~3 kcal/mole). Le mécanisme de post-polymérisation en phase solide est donc similaire au processus en phase liquide et diffère de celui de la polymérisation en phase solide au cours de l'irradiation. Ces faits sont une évidence pour la spécificité de la polymérisation induite dans l'état solide au cours de l'irradiation. L'efficience élevée d'une telle polymérisation est probablement due à la formation d'états moléculaires excités de courte durée de vie. De tels états disparaissent aussitôt après la fin de l'irradiation à l'état solide (quoique le signal RSE persiste); en phase liquide leurs concentrations stationnaires au cours de l'irradiation sont beaucoup plus basses par trite de l'augmentation de la vitesse de désactivation. De tels centres actifs peuvent être beaucoup plus efficaces que les ions ou radicaux, pour la propagation de chaîne énergétique de la polymérisation à l'état solide comme l'a suggéré Semenov.

Zusammenfassung

Die strahlungs-induzierte Polymerisation von festem und flüssigen Acrylnitril (AN) wurde bei −196 bis 0°C untersucht. Zur Entscheidung, ob Polymerisation im festen Zustand während der Bestrahlung oder während der darauffolgenden Erwärmung statt-

findet, wurde eine diathermes Kalorimeter benützt. Die Gegenwart aktiver Zentren während der Bestrahlung bei verschiedenen Temperaturen und ihr Verschwinden nach der Bestrahlung wurde nach der ESR-Methode festgestellt. Auch die Kinetik der Nachpolymerisation wurde untersucht. In AN findet Polymerisation in fester Phase bei weniger als −140°C nur während der Bestrahlung statt. Es besteht eine gewisse Grenze für die Polymerausbeute und trotz Weiterbestehens der Gestalt und Intensität des ESR-Signals nach Beendigung der Bestrahlung werden keine Nacheffekte beobachtet. Die Aktivierungsenergie der Polymerisation von AN in fester Phase ist bis zum Schmelzpunkt (−82°C) gleich Null. Bei höheren Temperaturen als −140°C besteht für die Ausbeute an AN-Polymeren keine Grenze mehr und es findet Nachpolymerisation statt, deren Aktivierungsenergie (∼3 kcal/Mol) die gleiche wie bei der Polymerisation in flüssiger Phase ist. Der Mechanismus der Nachpolymerisation in fester Phase ist daher demjenigen des Prozesses in flüssiger Phase ähnlich und unterscheidet sich von dem der Polymerisation in fester Phase während der Bestrahlung. Diese Umstände bilden einen Beleg für die Spezifität der strahlungs-induzierten Polymerisation in fester Phase während der Bestrahlung. Die hohe Ausbeute bei dieser Polymerisation wird wahrscheinlich durch die Bildung kurzlebiger angeregter Molekülzustände verursacht. Solche Zustände klingen bald nach Beendigung der Bestrahlung in fester Phase ab (obgleich das ESR-Signal bestehen bleibt) und in flüssiger Phase ist ihre stationäre Konzentration während der Bestrahlung wegen der höheren Löschgeschwindigkeit viel niedriger. Solche aktive Zentren können nach der Ansicht von Semenov bei der Energiekette der Polymerisation in fester Phase viel wirksamer sein als Ionen oder Radikale.

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Radiation-Induced Solid-Phase Polymerization. II. Polymerization of Vinyl Acetate

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I. INTRODUCTION

In continuing a systematic investigation of radiation-induced solid-phase polymerization, we have undertaken a detailed study of vinyl acetate polymerization, together with correlation of values for various temperature dependences of polymerization rates.[1] The vinyl acetate (VA) studied, $CH_2{=}CHOOCH_3$ (m.p. −93°C., b.p. +72.5°C.), appeared to provide a convincing example of the specific radiation-induced polymerization in the course of irradiation. The radiation-induced polymerization of this monomer was not studied before, but its polymerization under the action of various radical initiators was investigated rather extensively.[2] The mechanism of VA polymerization is considered to be a typical radical process. At low temperatures (below −129°C.) VA may occur in a crystalline and in a glasslike form (unstable within this temperature range). This opens up additional possibilities for studying the effect of structural factors on polymerization kinetics.

In order to find out whether the regularities observed for AN and VA were general, and to establish the nature of the relationship between the temperature dependence and the capacity of monomers to polymerize by a radical or by a ionic mechanism, the initial rates of liquid-state and solid-state polymerization of various monomers other than AN and VA were studied as functions of temperature.

II. EXPERIMENTAL

The monomers studied were irradiated with 1.6 m.e.V. electrons using an accelerator designed at the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences. A general description of the experimental technique was given in Part I.[3] Consequently, only some details specific for different monomers will be considered here (Table I).

Vinyl acetate monomer was dried with calcined sodium sulfate and distilled in a rectification column with 50 theoretical plates. The distilled VA was freed from air in a vacuum apparatus and then frozen into a silica vessel, where it was polymerized by ultraviolet irradiation up to 5–10%

TABLE I
Physical Constants of Polymers Used

Monomer	b.p., °C.	m.p., °C.
Methyl methacrylate (MMA)	180	−48
Vinyl acetate (VA)	72.5	−93
Acrylonitrile (AN)	78.5	−82
Phenylacetylene (PA)	142	−40
Formaldehyde (FA)	21	−92
Isobutene (IB)	−6.9	−140

conversion. Then the vessel containing the partly polymerized VA was connected to the vacuum apparatus, and the monomer was condensed into a calibrated flask. The cells for irradiation and the technique used for filling these up were similar to those described previously.[1] At low temperatures VA may occur both in a glasslike and in a crystalline state. To obtain the glasslike state the cell for irradiation was rapidly frozen with liquid nitrogen. A fine crystalline state was attained by keeping the cell, previously frozen at −196°C. in a thermostat, at −110 to −120°C. for 10–15 min. Large crystals were obtained by slow cooling of the VA-containing cell to the melting point, and then keeping it at −100°C. for a long time. The polyvinyl acetate viscosities were determined, and the molecular weights were calculated by use of the equation:[4]

$$[\eta] = 2.2 \times 10^{-4} \bar{M}^{0.67}$$

The techniques for irradiation, thermostatting, dosimetry, and calorimetric measurements were described previously.[1] The accumulation of active centers during the VA irradiation was studied by the ESR method, as in the case of AN.[3]

In view of the very high radiation-induced yield in formaldehyde (FA), this monomer was irradiated not with a direct beam of electrons, but with bremstrahlung, behind a tungsten screen. Absolute dosimetry was not applied; data on temperature dependence with respect to the dose were normalized over Magat's results.[5]

The technique used for purification of isobutene (IB) was described previously.[6]

The technique for phenylacetylene purification has also been described.[7]

III. EXPERIMENTAL RESULTS

Kinetic curves for the initial step of radiation-induced VA polymerization in the liquid and solid phase are shown in Figures 1 and 2. The solid-phase polymerization of VA proceeds at considerably lower rates than for AN. The rate of polymerization of the crystalline VA (especially so for large crystals) is lower than for the glasslike form.

The initial rate of polymerization of glasslike VA is proportional to the first power of the radiation intensity, I (Fig. 3), while for the liquid phase.[8]

$V^0 \sim I^{0.5}$. The activation energy for solid-phase polymerization tends to zero over the whole temperature range: from −196°C. to the phase transition point (−129°C.) for glasslike VA, and to the melting point (−93°C.) for crystalline VA (Fig. 4).

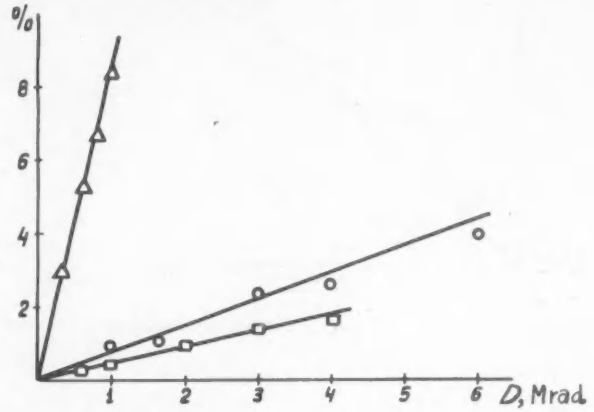

Fig. 1. Kinetic curves for VA polymerization in the liquid phases (I = 0.2 Mrad/min.) at (△) 0°C.; (○) −60°C.; (□) −90°C.

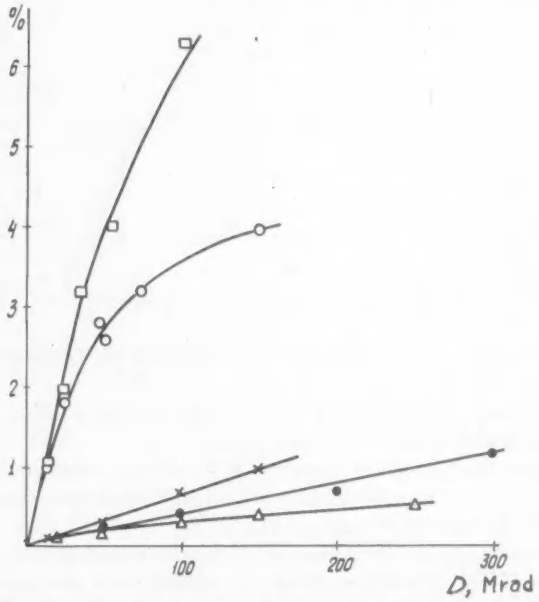

Fig. 2. Kinetic curves for VA polymerization in the solid phase (I = 5 Mrad/min.): (□) −150°C., glass form; (○) −196°C., glass form; (×) −170°C., crystals; (●) −120°C., crystals; (△) −196°C., crystals.

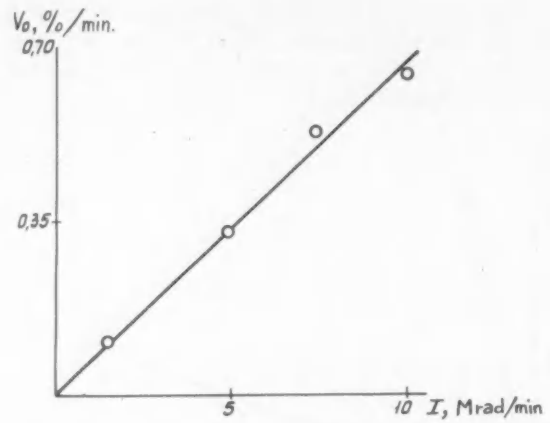

Fig. 3. Initial rate of glasslike VA polymerization as a function of radiation intensity (at −196°C.).

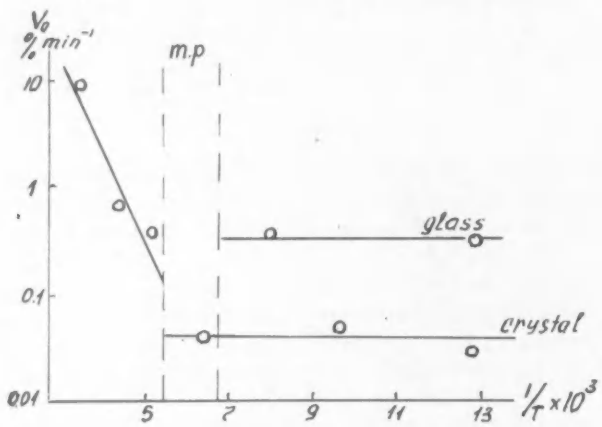

Fig. 4. Initial rate of VA polymerization as a function of temperature.

The activation energy for the liquid-phase radiation-induced polymerization is 3.7 kcal./mole.

Solid-phase VA post-polymerization is observed at none of the temperatures studied, both for the crystalline and for the glasslike state, contrary to what is observed for AN[1] and acrylamide.[9]

The molecular weight of polyvinyl acetate as a function of the dose for irradiation of the glasslike monomer at −150°C. is shown in Figure 5. Though the absolute values for average molecular weights of polyvinyl acetate may appear to be slightly overrated, as the low-molecular fractions are not allowed for with the technique used (pumping out of the monomer

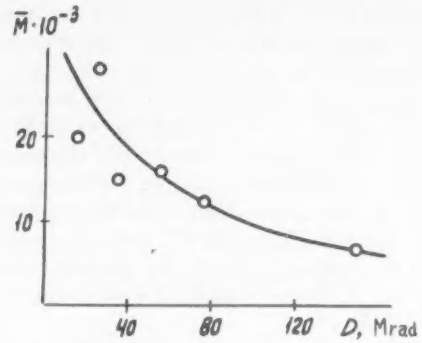

Fig. 5. Molecular weight of polyvinyl acetate as a function of the radiation dose (at −150°C. and I = 5 Mrad/min.).

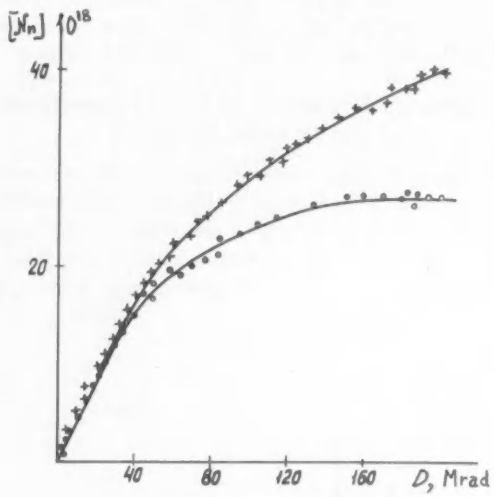

Fig. 6. Kinetic curve for the accumulation of active centers in solid VA during irradiation (I = 1 Mrad/min.): (+) −173°C.; (○) −150°C.

in vacuum), this cannot be of importance for the ratio of molecular weights determined for different doses. At the same dose (25 Mrad) the molecular weight of the glasslike VA polymer ($\bar{M} \sim 5000$) will be several times higher than for the crystalline form ($\bar{M} < 1000$). It was mentioned above that the glasslike state is obtained by fast freezing of vinyl acetate to −196°C., while an exothermic nonequilibrium transition from the glasslike to the crystalline state takes place at −129°C. Calorimetric measurements show that 34 ± 1 cal./g. of heat is liberated by this transition. The heat of melting of VA was shown to be 33 ± 2 kcal./g., and the heat of its poly-

merization is −248 cal./g.[10] If the whole 5% of the monomer converted into polymer (at −150°C. and D = 70 Mrad) were to undergo polymerization at the phase-transition or at the melting point, either an increase in the phase transition heat, or a decrease in the heat of melting by 12 cal./g. would be expected. However, in heating the glasslike VA irradiated with the dose mentioned, the heat values remain the same (within experimental error) as for nonirradiated samples. Consequently, there is no polymerization at the phase-transition or at the melting point. As no post-effect is observed even at −120°C., uniform development of polymerization during the heating is out of the question. Consequently, the polymerization of VA should be considered as occurring in the solid phase only during the irradiation.

The curves for accumulation of active centers during the irradiation at −173 and −150°C., as obtained by the ESR technique,[11] are shown in Figure 6. Measurements of active center concentrations in an irradiated and heated VA sample have shown that the initial concentration persists up to the melting point (as well as the ESR signal shape), and drops to zero with transition from the glass to the crystalline form.

Temperature Dependence of Initial Polymerization Rates for Other Monomers

The initial liquid-phase and solid-phase polymerization rates as functions of temperature are shown in Figures 7–10 for the four monomers listed in Table I (PA, MMA, FA, IB). The kinetic curves were obtained for the same radiation intensity. The temperature dependence of the liquid-phase polymerization rate for MMA and FA appears to be normal, as is the case

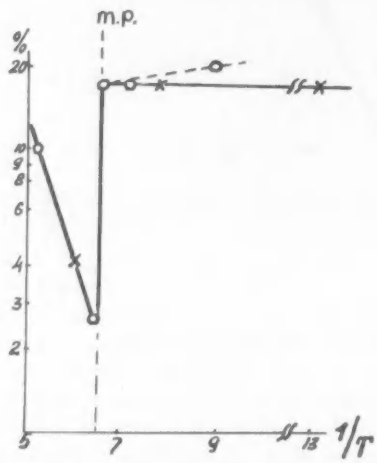

Fig. 7. Initial polymerization rate as a function of temperature for PA (I = 5 Mrad/min.).

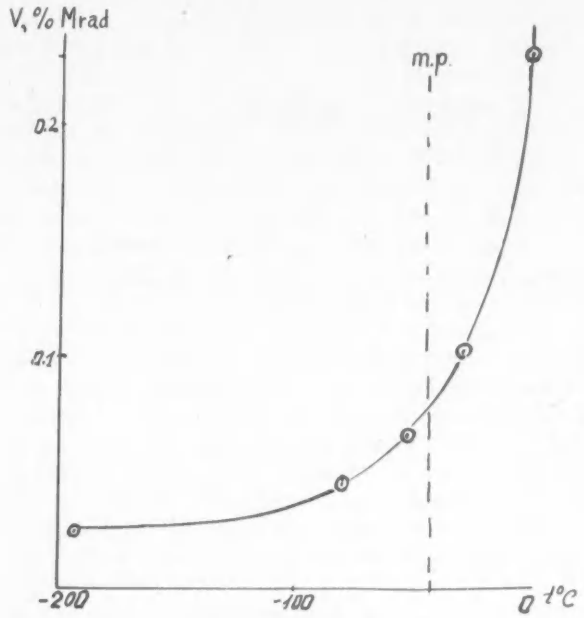

Fig. 8. Initial polymerization rate as a function of temperature for MMA (I = 0.75 Mrad/min.).

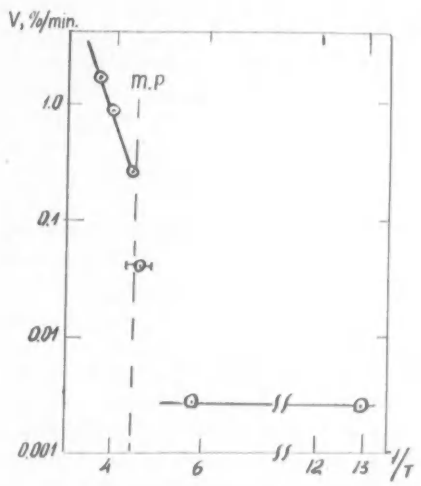

Fig. 9. Initial polymerization rate as a function of temperature for FA (I = 13 Mrad/min.).

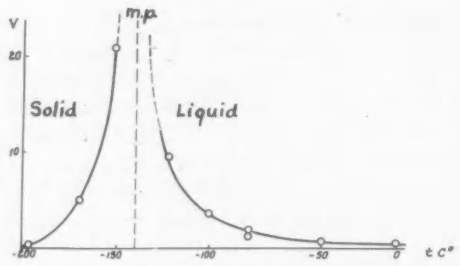

Fig. 10. Initial polymerization rate as a function of temperature for IB (I = 1 Mrad/min.).

for AN and VA (E = 4.25 kcal./mole for MMA,[12] and 2.3 kcal./mole for FA[5]), while for the solid phase the activation energy tends to zero. Isobutene is a characteristic example of another common type of temperature dependence with a maximum somewhere about the melting point. For IB in the liquid phase $E = -2.5$ kcal./mole, and in the solid phase $E \backsimeq +2$ kcal./mole. A low activation energy ($E = \pm 0.7$ kcal./mole) is observed for PA both in the liquid and in the solid phase over the whole temperature range of -196 to $+85$°C.

IV. DISCUSSION

Comparison of data on the temperature dependence of the initial rate of solid-phase polymerization for various monomers shows the occurrence of two main types of this dependence.

VA, AN, MMA, and FA belong to the type involving a positive activation energy for the liquid phase, and $E \backsimeq 0$ for the solid phase. The difference in shapes of the polymerization-rate drop at melting points is of secondary importance, as for a general case (i.e., when the rate dependence versus the intensity of radiation is different for the solid and liquid phase) it will depend on the radiation intensity. Of importance is the fact that at all intensities considered the initial solid-phase polymerization rate is constant over a wide temperature range.

It was shown by calorimetric measurements for acrylonitrile[1] and VA that solid-phase polymerization occurs in the course of irradiation. Consequently, the absence of temperature dependence for the polymerization rate may be due to the same reasons, as those discussed previously for acrylonitrile.[3]

The second main type of temperature dependence is illustrated by our experiments with isobutene. A maximum polymerization rate close to the melting point (due to the fact that the activation energy for polymerization is negative for the liquid and positive for the solid phase) is characteristic for a number of monomers polymerizing solely by the ionic mechanism (hexamethyl-cyclotrisiloxane,[13,15] trioxane, β-propiolactone, and other cyclic monomers[15]).

Increase in the rate of liquid-phase IB polymerization with decreasing temperature seems to be due to a high temperature coefficient of chain termination, i.e., to increase in the lifetimes of ions with cooling of the liquid.[16] This is common for many ionic processes.

However, it is striking that a normal temperature dependence of the reaction rate is observed for the solid phase, while the ionic mechanism would be natural for this type of polymerization as well. Moreover, a very fast drop in the liquid-phase reaction rate with increase in temperature (up to zero) was observed in all experiments involving inversion of the activation energy sign at the melting point,[13–15] so that there can be no question of a certain activation energy value for liquid-phase polymerization. This suggests that some particular part is played by the melting point, its influence being exerted both on the solid and the liquid phases. A detailed study of reactions involving a temperature dependence of this kind would be of extreme interest for the elucidation of this striking and seemingly rather frequent phenomenon. In particular, calorimetric investigations would be of great use in determining what is the role of polymerization in the course of irradiation, and to establish the post-effect for monomers displaying this kind of temperature dependence. The third type of the polymerization rate–temperature dependence observed for PA seems to be infrequent, and an explanation for it was suggested before.[7]

VA polymerization is similar to that of acrylonitrile discussed in the previous paper[1] in that it proceeds in the course of irradiation (especially so for VA, as post-polymerization effects are absent) and terminates after the radiation is cut off, though the ESR signal intensity and shape persist. It was mentioned above that liquid-phase VA polymerization is characteristic for a purely radical process. Consequently, in spite of the persistence of active centers showing ESR signals, the absence of post-effects in the solid phase is convincing evidence that purely radical polymerization of the common type does not occur in the solid phase. As polymerization in the course of irradiation, it may be due to the same reasons that were discussed in Part I,[3] i.e., to short-lived excited states, and to "loosening" of the substance. The complete absence of post-effects for VA makes it the most convincing example of the specificity of polymerization in the course of irradiation. An essential difference in the solid-phase polymerization of VA and acrylonitrile is that for VA the limiting polymer yield is not attained. Another interesting peculiarity of VA polymerization is the marked decrease in the reaction rate and molecular weight of the polymer in transition from the crystalline to the glasslike state of the monomer. This was not observed for cyclic monomers.[15] These two peculiarities seem to be related to the ratio of the monomer to polymer crystalline structures, and with the possible importance of a "preorientation" of the polymer in the monomer subjected to irradiation. Proportionality of the polymerization rate to the first power of radiation intensity, commonly characteristic of solid-phase polymerization, is evidence that chain termination is not a function of interaction between the growing polymer chains, but

may be due either to defects or admixtures, or else to dissipation of energy by growing energy chains.

V. SUMMARY

The radiation-induced polymerization of vinyl acetate (VA) was studied for the liquid and the solid phase (glasslike state, and both fine and large-grained crystalline states) over the temperature range of −196 to 0°C.

The activation energy for VA polymerization is $E = 3.7$ kcal./mole for the liquid phase and $E = 0$ for the solid phase (the absolute rate of polymerization of glasslike VA being higher than that of the crystalline form by about a power of ten).

Contrary to what was observed for acrylonitrile, for VA an increased radiation dose does not result in the occurrence of a certain limiting polymer yield. The molecular weight of the polymer formed decreases with increasing dose, just as for acrylonitrile.

Post-polymerization of VA in the solid phase was observed at none of the temperatures below the melting point (−93°C.), in spite of the persisting shape and intensity of the ESR signal and of the long lifetimes of ions in the solid phase at low temperatures.

Direct calorimetric measurements show that VA polymerization occurs solely in the course of irradiation, and not in the subsequent heating (for instance, not at the glass–crystal transition point, at −129°C.).

Solid- and liquid-phase investigations on the temperature dependence of the initial polymerization rate for a number of monomers, such as methyl methacrylate, formaldehyde, isobutene, and phenylacetylene, show that for the first two the temperature dependence was of the same nature as for acrylonitrile and VA ($E \approx 0$ in the liquid phase, $E > 0$ in the solid phase). For isobutene and other monomers polymerizing by a purely ionic mechanism, $E > 0$ for the solid phase and $E < 0$ for the liquid phase. This results in a maximum polymerization rate close to the melting point.

A low positive activation energy is observed for phenylacetylene over the whole temperature range from −196 to +85°C., both for the liquid and the solid phase.

These data are evidence for the specificity of solid-phase polymerization in the course of irradiation. Such polymerization may be favored by the formation of short-lived excited states participating in the development of energy chains, by the motion of molecules upon electron impact, the defreezing of rotation, and the excitation of molecular vibrations along tracks of primary and δ-electrons.

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Synopsis

The radiation-induced polymerization of vinyl acetate (VA) was studied in the liquid phase and two solid phases (glasslike and crystalline) over the temperature range of −196 to 0°C. A calorimetric technique was used to determine whether polymerization takes place in the solid state or during subsequent heating; the presence of active centers during irradiation and their disappearance after irradiation was followed by the ESR method. Post-polymerization kinetics were also studied. The activation energy for VA polymerization of is 3.7 kcal./mole for the liquid phase and zero for the solid phase. No post-effects occur in the solid state for VA up to the melting point. Unlike the case with acrylonitrile, an increased radiation dose does not result in the occurrence of a limiting polymer yield. In crystalline, as well as in the glassy state the polymerization of VA takes place only during irradiation, without activation energy, and ends with the switching off of the beam, in spite of the persistence of the shape and intensity of the ESR signal. Solid-state and liquid-phase investigations on the temperature dependence of polymerization rate for methyl methacrylate, formaldehyde, isobutene, and phenylacetylene show that for the first two the temperature dependence is of the same nature as for VA and acrylonitrile. For isobutene, there is a maximum polymerization rate close to the melting point. A low activation energy is observed for phenylacetylene over the whole temperature range from −196 to +85°C. for both solid and liquid phases. These data support the concept of specificity of solid-state polymerization during irradiation. Such polymerization may be favored by formation of short-lived excited states participating in the development of energy chains, by the motion of molecules upon electron impact, the defreezing of rotation, and excitation of molecular vibrations along tracks of primary and δ-electrons.

Résumé

On a étudié la polymérisation de l'acétate de vinyle (AV) induite par radiation en phase liquide et deux phases solides (pseudo-vitreuse et cristalline) sur une gamme de températures allant de −196° à 0°C. En vue de déterminer si la polymérisation avait lieu soit dans la phase solide soit durant le chauffage subséquent, on a utilisé une technique calorimétrique; la présence de centres actifs au cours de l'irradiation et leur disparition après irradiation ont été suivies par la méthode de RSE. La cinétique de post-polymérisation a également été étudiée. L'énergie d'activation de polymérisation pour l'AV est de 3,7 kcal/mole dans la phase liquide et zéro dans la phase solide. Aucun effet postérieur n'a lieu dans l'état solide pour l'AV jusqu'au point de fusion. Contrairement au cas de l'acrylonitrile, une dose croissante de radiation ne donne pas lieu à une limitation du rendement en polymère. Dans l'état cristallin aussi bien que dans l'état vitreux la polymérisation de AV n'a lieu que durant l'irradiation, sans énergie d'activation et cesse en arrêtant le faisceau en dépit de la persistance de la forme et de l'intensité du signal de RSE. Des études en phase solide et en phase liquide concernant la relation qui lie la température et la vitesse de polymérisation pour le formaldéhyde, l'isobutène et le phényl-acétylène montrent que pour ces deux premiers, la dépendance de la température est la même que celle de l'AV et l'acrylonitrile. Pour l'isobutène il existe une vitesse de polymérisation maximum proche du point de fusion. On observe une faible énergie d'activation pour le phénylacétylène sur toute la gamme de températures de −196 à 85°C pour les phases solides et liquides. Ces résultats étayent le concept de la spécificité de la polymérisation en phase solide au cours d'irradiation. De telles polymérisations peuvent être favorisées par formation d'états d'excitation à courte durée de vie participant au développement de chaînes énergétiques par le mouvement des molécules sous l'impact électronique, le "dégel" de rotation et l'excitation de vibrations moléculaires le long du chemin d'électrons primaires et δ.

Zusammenfassung

Die strahlungs-induzierte Polymerisation von Vinylacetat (VA) wurde in flüssiger Phase und in zwei festen Phasen (glasartig und kristallin) im Temperaturbereich von −196 bis 0°C untersucht. Der Nachweis der Polymerisation im festen Zustand oder bei der nachherigen Erwärmung erfolgte mit einem kalorimetrischen Verfahren; das Vorhandensein aktiver Zentren während der Bestrahlung und ihr Verschwinden nach der Bestrahlung wurde ESR-spektroskopisch nachgewiesen. Auch die Kinetik der Nachpolymerisation wurde untersucht. Die Aktivierungsenergie der VA-Polymerisation in flüssiger Phase beträgt 3,7 kcal/Mol; in fester Phase ist sie Null. Bis zum Schmelzpunkt treten bei VA im festen Zustand keine Nacheffekte auf. Ungleich den Verhältnissen beim Acrylnitril führt die Erhöhung der Strahlungsdosis nicht zum Auftreten einer Ausbeutegrenze für das Polymere. Im kristallinen und im Glaszustand findet die Polymerisation von VA nur während der Bestrahlung und ohne Aktivierungsenergie statt und ist mit dem Abschalten des Strahles, trotz des Weiterbestehens der Gestalt und Intensität des ESR-Signals, beendet. Untersuchung der Temperaturabhängigkeit der Polymerisationsgeschwindigkeit von Methylmethacrylat, Formaldehyd, Isobuten und Phenylacetylen zeigt, dass bei den ersten beiden die Temperaturabhängigkeit von gleicher Natur wie bei VA und Acrylnitril ist. Bei Isobuten besteht in enger Nachbarschaft des Schmelzpunktes ein Maximum der Polymerisationsgeschwindigkeit. Für Phenylacetylen wird im ganzen Temperaturbereich von −196° bis +85°C in fester und flüssiger Phase eine niedridge Aktivierungsenergie festgestellt. Diese Ergebnisse bestätigen das Konzept der Spezifität der Polymerisation in fester Phase während der Bestrahlung. Eine solche Polymerisation kann durch die Bildung kurzlebiger angeregter Zustände, die an der Entwicklung von Energieketten teilnehmen, begünstigt werden, sowie durch die Bewegung der Moleküle nach dem Elektronenstoss, das Erwachen der Rotation und die Anregung von Molekülschwingungen in den Spuren der primären und δ-Elektronen.

Discussion

A. Chapiro (*Bellevue, France*): Je ne pense pas que l'on puisse conclure sur la base de la seule constatation d'énergies d'activation semblables que le même mécanisme a lieu dans la polymérisation de l'acrylonitrile pendant l'irradiation en phase liquide et pendant la post-polymérisation en phase solide. En effet, ces deux énergies d'activation sont en réalité des grandeurs très complexes. En phase liquide, le polymère prècipite au cours de la réaction et la cinétique s'en trouve très compliquée. En phase solide, des processus comme la diffusion (ou le déplacement) des molécules de monomère et des chaînes croissantes ont certainement un coefficient de témperature élévé et l'énergie d'activation globale ne peut être interprétée d'une manière simple. Nous avons également trouvé pour la post-polymérisation en phase solide une énergie d'activation globale de 3 lr cal/mole (*J. Chim. Phys.*, **59,** 537 (1962)) tandis qu'en phase liquide l'énergie d'activation est sensiblement plus élevée, de l'ordre de 13 cal/mole (*J. Polymer Sci.*, **48,** 167 (1960)). Par ailleurs, nous avons trouvé, contrairement à Barkalov et coll., que la vitesse de la post-polymérisation entre $-140°$ et $-90°$ n'est pas constante mais décroit avec la conversion. La vitesse initiale de la post-polymérisation à $-90°$ est rrès voisine de la vitesse pendant l'irradiation ce qui suggère que ce sont ces deux réactions qui procèdent par un même mécanisme (voir également la communication de Bensasson et coll. à ce Symposium).

N. A. Plate (*U.R.S.S.*): Je ne suis pas l'auteur de cette communication, mais en ce qui concerne mon opinion personnelle, je pense qu'il existe quelques paramètres communs pour les polymèrisations en phase liquide et en phase solide. Pour èlucider les particularités des mécanismes des polymérisations à l'état solide, il faut trouver des caractéristiques communes.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 923–934

Investigations in the Field of Radiation-Induced Solid-State Polymerization

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Much experimental work is yet to be done in the field of radiation-initiated solid-state polymerization before a general theory can be established. Some generalizations published previously[1–5] can be considered as reviews rather than theories of general validity.

The effect of crystalline structure on the polymerization kinetics and on the polymer structure is surely one of the most interesting problems in radiation-induced solid-state polymerization.

In the present paper new experimental results and probable interpretations are presented on the field of solid-state polymerization of some monomers which have not previously been investigated.

Cetyl Methacrylate

As shown by Chapiro,[6] no polymerization can be observed in pure methyl methacrylate when irradiated in the solid state. If, however, paraffin oil is added, the monomer does polymerize fairly well. Cetyl methacrylate (melting point 15°C.), having a long paraffin chain, can be considered in some respects to be a 1:1 mixture of methyl methacrylate and paraffin oil within a single molecule.

An Arrhenius plot of the radiation-induced polymerization of cetyl methacrylate is shown in Figure 1. In the liquid phase (60, 40, and 20°C.) the usual linear relationship is obtained with an over all activation energy of 2.5 kcal./mole. The measured values of the polymerization rates are proportional to the square roots of the dose rates. $G_{in} = 0.68$ monomer/100 e.v. can be calculated. Near the melting point an interesting phenomenon can be observed. The polymerization rate versus temperature curves exhibit a sudden break near the melting point (10°C.), reaching a higher value then at 60°C. The activation energies also change rapidly in this portion. The polymerization rate is proportional to the 1.2 power of the dose rate.

In the solid state, farther away from the melting point (at temperatures of −21, −78, and −195°C.) the polymerization rate increases monotonously as temperature is decreased. The overall activation energy of

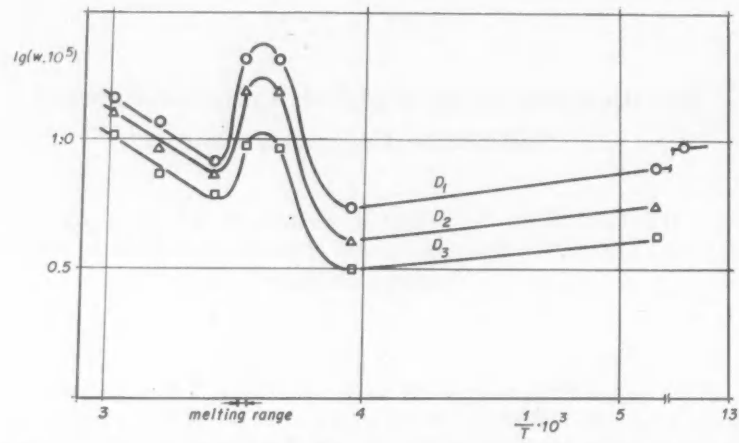

Fig. 1. Temperature dependence of the polymerization rate of cetyl methacrylate at various dose rates: (○) D_1 = 16,000 r/hr.; (△) D_2 = 13,100 r/hr.; (□) D_3 = 8,800 r/hr.

the process is −0.7 kcal./mole; the polymerization rate is proportional to the dose rate.

Besides being affected by the chemical structure and reactivity of the monomer, the solid-state polymerization is very likely determined by the crystalline structure. If the monomer molecules are arranged in the crystal lattice in a favorable way, polymerization can proceed in the solid state even at very high rates. (In the case of cetyl methacrylate, the polar methacrylic acid groups are most likely oriented parallel to each other and so are the cetyl substituents.)

In the case of cetyl methacrylate near the melting point, however, in the solid state, thermal agitation might result in a packing close enough for the monomer groups to overcome the deformation barrier. Since the groups are prearranged in a favorable way in the crystalline lattice, the number of favorable collisions might be enormously increased this way. This should explain the observed sharp increase of polymerization rates near the melting point.

The increase of the polymerization rates observed at −21°C. might be caused by a change in the crystalline structure of the monomer. Indeed, a phase transition point was observed at −16°C. by the method of differential thermal analysis.

It is very difficult to determine whether the polymerization mechanism is ionic in the solid state. If it is ionic, it should be anionic, for such cationic catalysts as $AlCl_3$ and $TiCl_4$ have proved to be ineffective. Addition of typical inhibitors (2%) as α-nitroso-β-naphthol and *p*-nitrosodimethylaniline, prevent the polymerization at 0°C. and at −78°C. on irradiation for 72 hr. at a dose rate of 16,000 r/hr. Under similar

conditions and in the absence of these additives, the conversion would reach its upper limit (60%). This would suggest a radical mechanism, if real inhibition took place.

Figure 2 shows the temperature and dose rate dependence of the average degrees of polymerization for the polymers obtained by the procedure

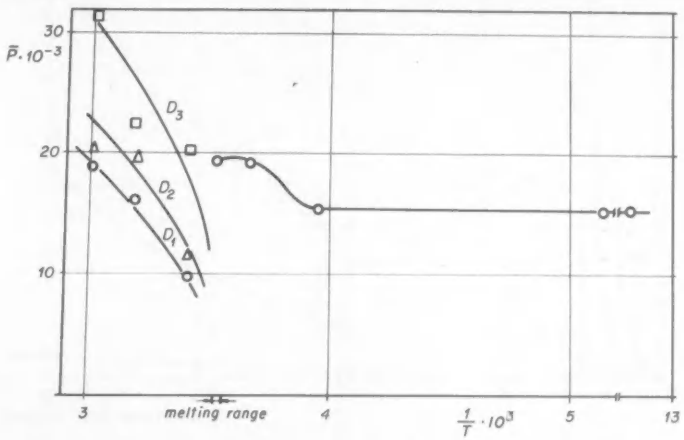

Fig. 2. Temperature and dose rate dependence of the molecular weights of poly(cetyl methacrylate). Symbols as in Fig. 1.

described above. In the solid state the degree of polymerization is practically independent of the temperature and the dose rate. This suggests that the chain lengths are mainly determined by crystalline properties, i.e., that chains can propagate until they reach a vacancy or a microcrystalline border surface.

N-Vinylsuccinimide

Figure 3 shows the polymerization kinetics of *N*-vinylsuccinimide (NVSI) at a constant dose rate as a function of the temperature. Figure 4 shows the effect of the dose rate on the kinetics at constant temperature at small conversions. The kinetic curves all have an accelerating character.

Figure 5 shows the solid-state polymerization kinetics at 40°C. and the variation of the temperature inside the monomer sample. Figure 6 shows the differential thermal effect of the polymerization on varying of the ampule diameters. It can be concluded from the data of Figures 5 and 6 that under the given experimental conditions the acceleration of the polymerization results in an increase of the inner temperature of the monomer sample. As a result of this, the thermal equilibrium of the system is destroyed, and the temperature of the monomer may even reach the melting temperature, resulting in an explosion-like phenomenon (thermal explosion). Similar behavior has not previously been observed in vinyl poly-

merization, being reported only in the polymerization of formaldehyde[7] and acetaldehyde.[8]

There is always a certain induction period τ_i before this explosion takes place. This can be characterized conventionally by the intersection of the

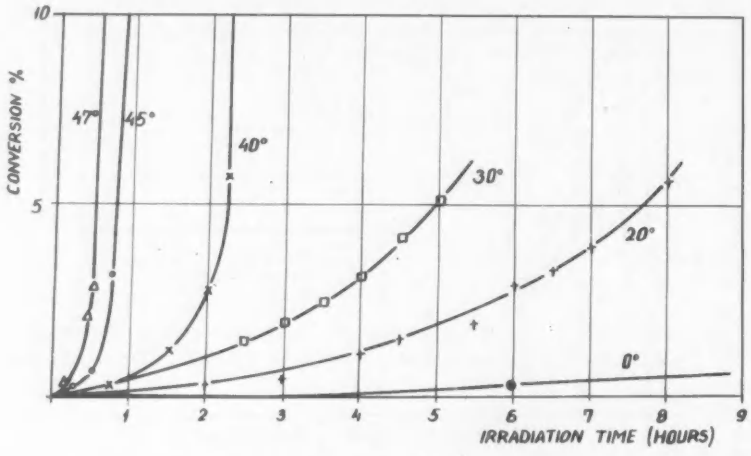

Fig. 3. Kinetics of polymerization of *N*-vinylsuccinimide at different temperatures and at constant dose rate (15,800 r/hr.)

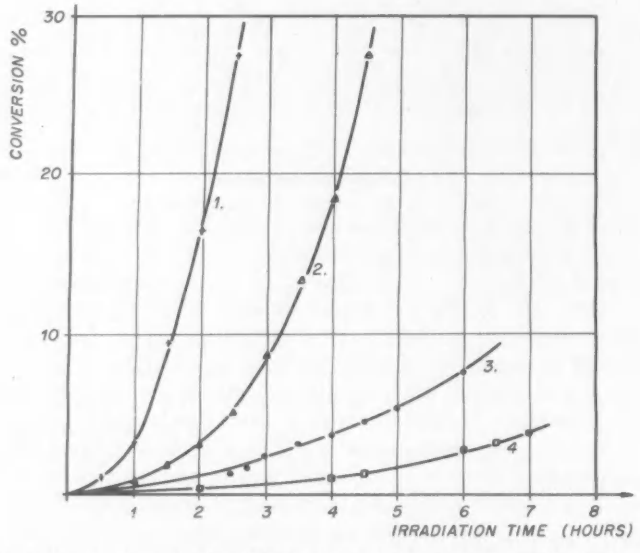

Fig. 4. Kinetics of polymerization of *N*-vinylsuccinimide at 20°C. at different dose rates: (*1*) 260,300 r/hr.; (*2*) 107,940 r/hr.; (*3*) 32,700 r/hr.; (*4*) 15,800 r/hr.

prolongation of the ascending portion of the curve and of the time base. The shape of the temperature increase (Δt) versus time curves and the induction period τ_i depend on the polymerization temperature, dose rate, and on the container dimensions. If these parameters are properly chosen, thermally steady-state conditions can be achieved. This is illustrated in Figure 7. This suggests that the acceleration is due to the increase of the radical concentration.

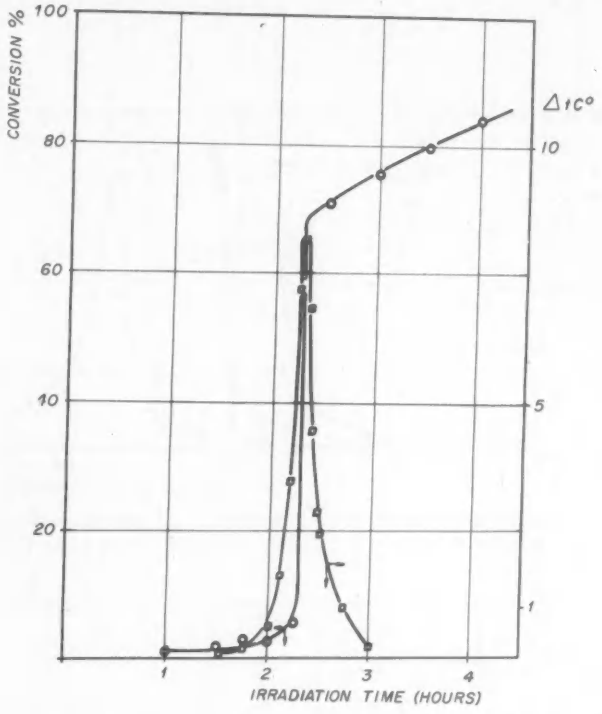

Fig. 5. Kinetics of polymerization of *N*-vinylsuccinimide at 40°C. at a dose rate of 15,800 r/hr. and the change of the temperature inside the monomer.

The temperature dependence of the induction period τ_i can be described by eq. (1):

$$\log \tau_i = (A/T) + C \tag{1}$$

where A is a constant which is connected with the activation energy of the polymerization, C is a constant which depends on the physical parameters of the irradiation, and T is the absolute temperature. There is a low temperature limit for the thermal explosion at about 20–30°C. in the present case.

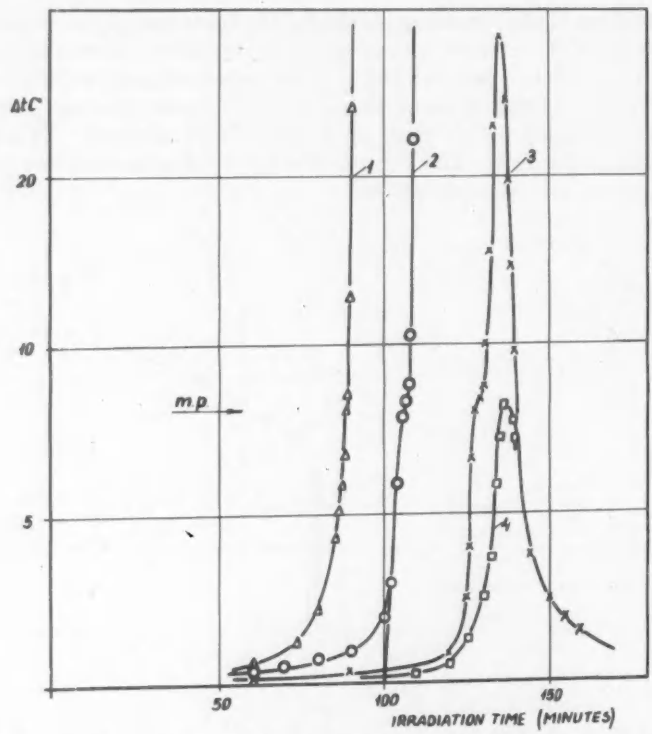

Fig. 6. The differential thermal effect of solid-state polymerization at 40°C. and a dose rate of 15,800 r/hr. with varying ampule diameters: (*1*) 32 mm.; (*2*) 24.5 mm.; (*3*) 12.4 mm.; (*4*) 6.2 mm.

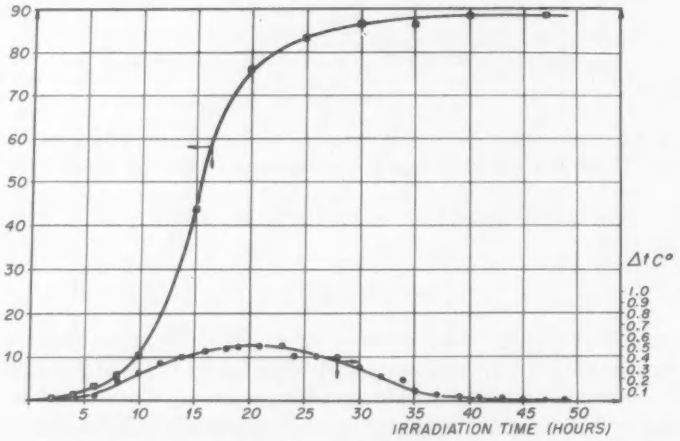

Fig. 7. Kinetics of polymerization of *N*-vinylsuccinimide at 20°C. at a dose rate of 15,800 r/hr. and the change of the temperature inside the monomer.

The dose rate dependence of the induction period at constant temperatures can be expressed as

$$\log \tau_i = B - n \log I \tag{2}$$

where B is a constant which depends on the parameters of the polymerization, n is the exponent of the dose rate in the conversion–dose rate dependence, and I is the radiation dose rate.

The kinetics of heterogeneous-phase polymerization (bulk and solution polymerization with precipitation) has been described by Magat[9] as follows:

$$-\ln (M/M_0) = (k_p/k_t) \ln \cosh [(k_a k_t I)^{1/2} t] \tag{3}$$

where M is the monomer concentration at time t; M_0 is the same at $t = 0$, k_a is the rate constant of the initiation, k_p is the rate constant of the propagation; k_t is the rate constant of the termination; I is the initiator concentration, or the dose rate.

At small conversions and if the cosh term in eq. (3) is small, instead of eq. (3) a simpler form can be derived:

$$\frac{\Delta M}{M_0} \cong 1/2\, k_a k_p I t^2 \tag{4}$$

This form will be used here in the following form:

$$X = K t^2 \tag{5}$$

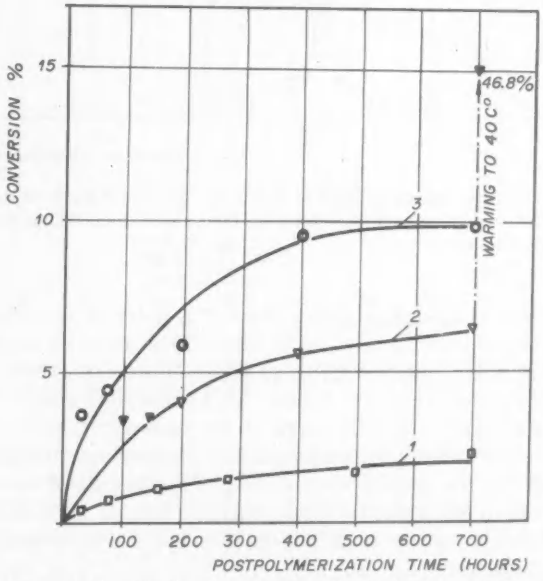

Fig. 8. Post-polymerization kinetics of *N*-vinylsuccinimide in the solid state at 0°C. with different radiation doses: (*1*) 94,600 r; (*2*) 283,800 r; (*3*) 378,400 r.

where X is the per cent conversion and $K = {}^1/_2\, k_a\, k_p\, I$ in per cent/hour^2. The dose rate dependence of the K values is not linear. K has been found to be proportional to the 1.3 power of the dose rate. It should be noted, however, that the instantaneous polymerization rates corresponding to 3% conversion are proportional to the 0.6–0.7 power of the dose rate.

For the post-polymerization investigations, irradiation was carried out at −78°C. at a dose rate of 15,800 r/hr. Under these conditions practically no polymerization takes place. The kinetics of the post-polymerization at 0°C. is shown in Figure 8, as a function of the preirradiation dose.

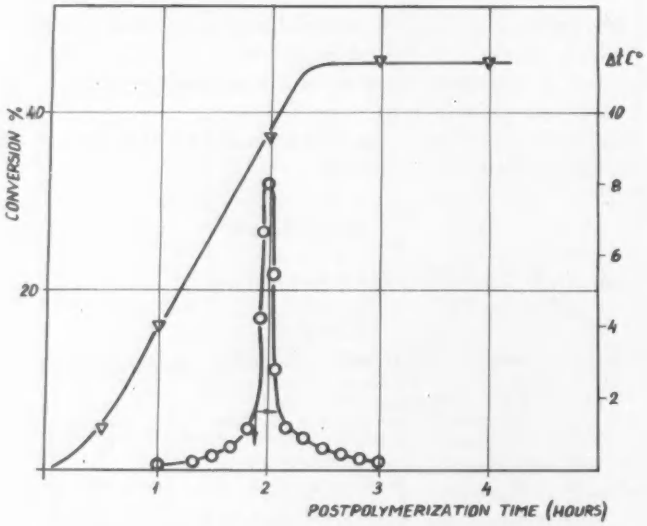

Fig. 9. Post-polymerization kinetics of *N*-vinylsuccinimide in the solid state at 40°C., 126,400 r radiation dose, ampule diameter of 6.2 mm., and with the change of the temperature inside the monomer.

After 700 hr. post-polymerization about 7% polymer is formed at 0°C. Heating a parallel sample up to 40°C. after 700 hr. standing results in an increase of the polymerization up to 46.8%. This means, that the lifetime of the active centers (radicals) is fairly high in the solid state.

Figure 9 shows the kinetic curve of the post-polymerization at 40°C. and the increase of the temperature inside the monomer during post-polymerization. In the post-polymerization, as in the case of radiation polymerization, two cases can be distinguished. One of them is the case of thermally steady-state polymerization (Fig. 8); the other one is the case of thermal explosion (Fig. 9).

By using the technique of the differential thermal analysis in the case of thermal explosions, the effect of additives (inhibitors) to the solid-state

polymerization could be investigated. The inhibition should result in a time-shift of the thermoanalytical curves, without, however, a change in their shape. If the inhibitor is ineffective in the solid state, the curves obtained with and without addition of inhibitor should coincide. The latter case is illustrated in Figure 10, where benzoquinone was used as inhibitor. The shift in the induction period is probably caused by the radiation protective behavior of the aromatic benzoquinone (energy transfer).

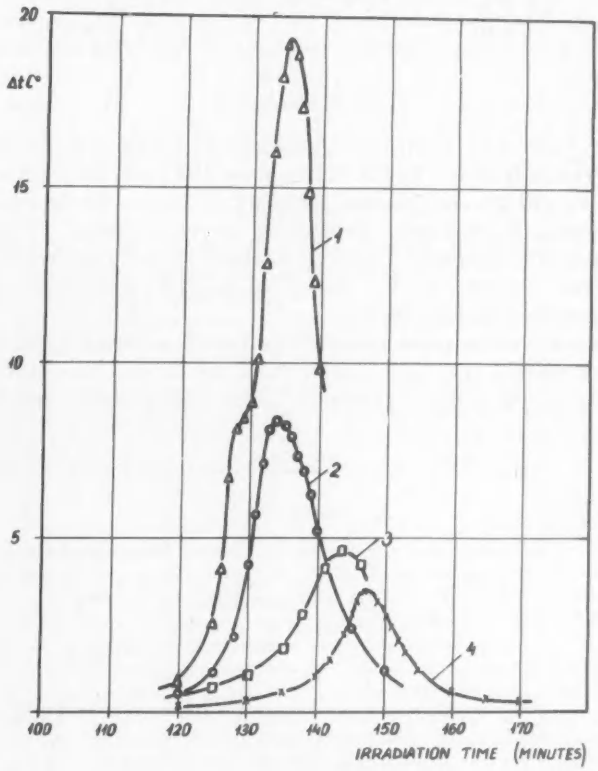

Fig. 10. Differential thermal analysis curves obtained in the presence of various concentions of benzoquinone: (1) 0%; (2) 0.1%; (3) 0.5%; (4) 0.93%.

The decrease in the thermal maximum is due to the decrease of the melting point as a result of the addition of the inhibitor. Benzoquinone is a typical inhibitor in the liquid state. In the solid state it cannot act as inhibitor because it is localized. Similar results were obtained in the case of DPPH.

The data collected in Table I show that in the case of thermal explosion most of the polymer is formed in the liquid phase.

TABLE I
Conversions in the Presence of Benzoquinone by DTA Measurements (Irradiation Time 3 hr., Temperature 4°C., Dose Rate 15,800 r/hr., Diameter of the Ampules 12.4 mm.)

Benzoquinone, wt.-%	Conversion, %
0	77.15
0.1	30.61
0.25	30.01
0.50	25.25
0.93	22.70

N-Vinylcaprolactam

Figure 11 shows the temperature dependence of the polymerization rate of *N*-vinylcaprolactam. In the liquid phase the usual decrease was observed with a brutto activation energy of 9 kcal./mole. In the solid phase the polymerization rate drops suddenly to a very low value. This might be caused by the unfavorable packing of the monomer groups in the solid phase. The over-all activation energy of the solid-state polymerization was found to be 14.7 kcal./mole.

If, however, the monomer is slowly supercooled, avoiding crystallization, the polymerization rates were found to be about 67 times more than in the solid state at the same temperature. The polymerization rates in the

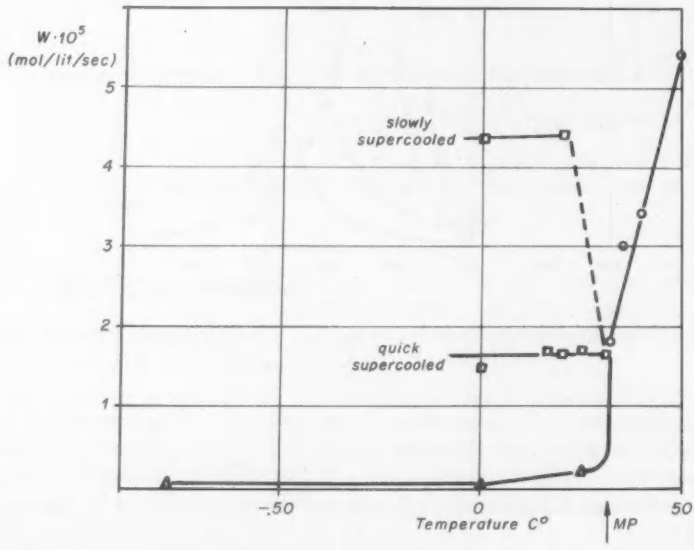

Fig. 11. Temperature dependence of the polymerization rate of *N*-vinyl caprolactam at a dose rate of 16.000 r/hr.

supercooled state show practically no temperature dependence between 30 and 0°C.

If the monomer is cooled rapidly down to −78°C., and then heated slowly to the temperature of polymerization, the polymerization rates become 27 times more than in the crystalline solid phase. The polymerization rates are also practically independent of temperature between 30 and 0°C.

The difference between the polymerization rates in the case of slow and rapid supercooling might be explained by assuming that in the case of slow supercooling a favorable prearranged structure is formed, which is different from the structure of the solid crystal. In the case of rapid supercooling a disordered state is fixed, which is more favorable for polymerization than the solid crystalline lattice, but less favorable than the structure formed by slow supercooling.

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Synopsis

Radiation polymerization kinetics of cetyl methacrylate, *N*-vinylsuccinimide and *N*-vinylcaprolactam have been investigated in the liquid and solid state. In the solid state each monomer exhibits a different temperature dependence of polymerization rate. This can be caused by the difference in the crystalline structures (different orientation of the monomer molecules in the lattice). In the solid-state polymerization and post-polymerization of *N*-vinylsuccinimide two cases can be distinguished depending on such parameters as temperature, dose rate, and sample dimensions: the case of thermal steady-state polymerization and the case of thermal explosion. *N*-Vinylcaprolactam polymerize very slowly in the solid state, while in the supercooled state quite high polymerization rates have been found. Slow supercooling results in polymerization rates about twice as high as fast supercooling does.

Résumé

Les cinétiques de polymérisation par radiation du méthacrylate de cétyle, de la *N*-vinyl-succinimide et de la *N*-vinyl-caprolactame ont été étudiées à l'état liquide et solide. A l'état solide chaque monomère présente une dépendance différente de la vitesse de polymérisation vis-à-vis de la température. Cela peut être provoqué par la différence dans les structures cristallines et par l'orientation différente des molécules de monomère dans le réseau. Lors de la polymérisation et de la post-polymérisation à l'état solide de la *N*-vinyl-succinimide, on peut distinguer deux cas qui dépendent de certains paramètres tels que la température, la vitesse de la dose et les dimensions de l'échantillon: le cas de la polymérisation thermique normale et le cas de l'explosion thermique. La

N-vinyl-caprolactame polymérise très lentement à l'état solide, tandis qu'à l'état supercongelé on a trouvé des vitesses de polymérisation considérablement élevées. Une supercongélation lente provoque des vitesses de polymérisation environ deux fois plus élevées qu'une supercongélation rapide.

Zusammenfassung

Es wurde die Kinetik der Strahlungspolymerisation von Cetylmethacrylat, *N*-Vinylsuccinimid und *N*-Vinylcaprolaktam in flüssigem und festem Zustand untersucht. In festem Zustand ist die Temperaturabhängigkeit der Polymerisationsgeschwindigkeit für jedes Monomere verschieden. Dies kann auf Unterschieden in der Kristallstruktur (verschiedene Orientierung der Monomermoleküle im Gitter) beruhen. Bei der Polymerisation und der Nachpolymerisation von *N*-Vinylsuccinimid in festem Zustand können zwei Fälle unterschieden werden, die thermische stationäre Polymerisation und die thermische Explosion. Welcher der beiden Fälle eintritt, hängt von gewissen Parametern, wie Temperatur, Dosisleistung und den Dimensionen der Probe ab. Während *N*-Vinylcaprolaktam in festem Zustand sehr langsam polymerisiert, treten im unterkühlten Zustand recht hohe Polymerisationsgeschwindigkeiten auf, und so führt langsames Unterkühlen zu einer etwa doppelt so grossen Polymerisationsgeschwindigkeit wie schnelles Unterkühlen.

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Polymer Fractionation Studies in the Solid-State Polymerization of Acrylamide Initiated by Gamma Radiation

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Introduction

Much of the detailed work on solid-state polymerization has been carried out on crystalline acrylamide (m.p. 84°C.) as monomer. Detailed kinetic studies were published on both the in-source and post-irradiation reactions of acrylamide.[1–4] The kinetics of such a system have been reported to be consistent with a bimolecular termination for post-polymerization reactions.[3,4] However, during the period of polymerization the radical concentrations measured by electron spin resonance were found to remain almost constant. This indicates that the characteristic bimolecular termination step observed in liquid-state polymerization is not involved in solid-state polymerization. The results obtained were consistent with the view that polymerization is a heterogeneous reaction, there being a nucleation mechanism in which the free radicals are probably trapped by overlapping of the growing polymer chains and favorable sites for nucleation of reaction are crystal imperfections.[1,2] The analysis of this reaction from the viewpoint of solid-state chemistry is supported by the evidence provided with x-ray diffraction[5,6] and optical microscopy.[2] Electron microscope studies on solid-state polymerization of acrylamide also supported the heterogeneous feature of this reaction.[7]

It was claimed, however, that the number of chains would be constant throughout the post-irradiation reaction and that consequently the initial free radical concentration could be calculated from the yield and molecular weight data.[3] It would be difficult to reconcile such a picture with the proposed nucleation mechanism. Consequently, fractionation studies were carried out on polymers made from monomers crystallized under vastly different preparative techniques with the hope that the resultant data might further clarify the issue.

Preliminary results on fractionation were submitted for publication earlier.[8]

Experimental

The acrylamide used was an American Cyanamid product. It was recrystallized three times from acetone, dried thoroughly in vacuum, and had a melting point of 84°C.

Propionamide was an Eastman Kodak product and was also recrystallized three times from acetone and dried under high vacuum. The melting point was 79°C.

Mixed crystals of acrylamide–propionamide were prepared by carefully weighing out the required amounts, mixing by grinding in a mortar, melting by heating to 90°C., and cooling quickly by immersion of the sample tube in a stream of cold water. This technique has been shown to yield mixed crystals in all proportions.[9]

Appropriate amounts of acrylamide and acrylamide–propionamide mixtures were measured into Pyrex tubes which were evacuated overnight at 10^{-4} mm. The tubes were sealed, weighed, and irradiations performed in the Brookhaven National Laboratory Co^{60} radiation sources.[10] Dosimetry measurements were performed by using the Fricke dosimetry method.[11]

The post-irradiation polymers was prepared by irradiating the monomer at −78°C. at appropriated conditions, immediately after irradiation, placing the sample tube in a constant temperature bath at 25.0°C. It was stored at this temperature for suitable time intervals for desired conversions.

The sample tubes were opened immediately after irradiation and the contents poured quickly into methanol. The mixture was stirred overnight and the precipitated polymer collected on a filter funnel and dried in a vacuum oven at room temperature to constant weight.

The polymeric samples were dissolved in water to produce 0.5% solution and fractionation was effected at 30.0°C. by addition of aliquots of methanol.

Intrinsic viscosities were measured in water solutions at 25.0°C.

Experimental Results and Discussions

Six polymeric samples were prepared under vastly different preparative techniques with the aim of fractionation. The preparation conditions of these samples are given in Table I. Complete analysis for fractionation was carried out at present with samples I, II, IV, and V.

The fractionation results for samples I and II were reported earlier.[8]

The results for the fractionation of the post-irradiation polymer, sample IV, which was obtained from a mixture 90% acrylamide and 10% propionamide monomer, are given in Table II. The molecular weights for the fractions are calculated from the intrinsic viscosities using the following relation which was given before for post-irradiation polymers:[8]

$$[\eta] = 4.07 \times 10^{-6} \bar{M}_n^{1.07}$$

The cumulative weight distribution curve is shown in Figure 1.

The results for the fractionation of the post-irradiation polymer at low conversion, sample V, are given in Table II. The molecular weights of fractions are again calculated using the above relation and the cumulative weight distribution curve shown in Figure 2.

TABLE I
Acrylamide Samples Prepared for Fractionation

Sample	Type of polymer	Dose, Mrad	Dose rate, Mrad/hr.	Irradiation temp., °C.	Polymerization temp., °C.	Conversion, %	Polymerization time, hr.
I	Post-irrad. acrylamide	0.80	0.257	−78	25.0	18.34	360
II	In-source irrad. acrylamide	2.46	0.410	27	27	95	6
III	In-source irrad. acrylamide	1.48	0.404	25	25	10.5	3.67
IV	Post-irrad. 90% acrylamide–10% propionamide	0.75	0.249	−78	25.0	20.5	26
V	Post irrad. acrylamide	0.74	0.245	−78	25.0	5.8	26
VI	Post irrad. acrylamide	0.75	0.249	−78	25.0	19.1	480

TABLE II
Fractionation Data for Post-Irradiation Acrylamide Polymer (Sample IV)

Fraction	Wt.% of fractions	$[\eta]$	$\bar{M}_v$
IV-1	1.19	1.322	142,000
IV-2	3.78	0.865	95,500
IV-3	4.53	0.858	94,200
IV-4	3.86	0.729	81,100
IV-5	6.56	0.690	77,100
IV-6	6.44	0.608	68,500
IV-7	1.01	0.542	61,700
IV-8	11.67	0.530	59,600
IV-9	7.88	0.507	57,700
IV-10	10.45	0.439	50,600
IV-11	15.08	0.420	48,400
IV-12	4.66	0.282	33,400
IV-13	9.73	0.280	33,200
IV-14	8.80	0.231	27,700
IV-15	4.36	0.186	21,700

It was reported[8] for the fractionation of sample I that 42 wt.-% of the polymer had essentially the same intrinsic viscosity and number average molecular weight. It is evident from Figures 1 and 2 that molecular weight distribution is much more broad for samples IV and V. This was caused in sample IV with the presence of propionamide since the conversions for sample I and IV are nearly the same, being 18.34 and 20.5 wt.-%, respectively. In the case of sample I, however, conversion is quite low being only 5.8 wt.-%.

In order to explain the occurrence of a significantly large percentage of polymer of constant molecular weight from the post-irradiation experiment a number of alternative suggestions were offered.[8] It seems reasonable to say that, the size to which any polymer chain grows is limited by the critical size of the crystal region in which the reaction is occurring. The possibility that all chains begin initiating polymerization simultaneously as

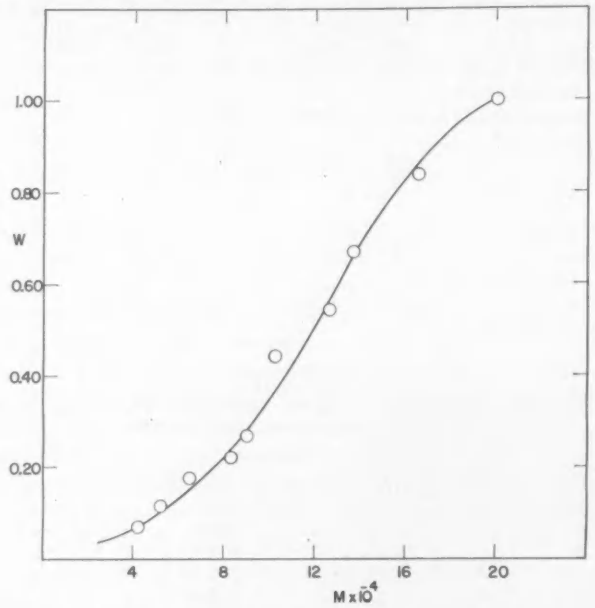

Fig. 1. Cumulative weight distribution for post-irradiation acrylamide polymer. Irradiation dose 0.75 Mrad at −78°C.; post-irradiation storage 26 hr. at 25°C.; conversion 20.5% (sample IV).

TABLE III

Fractionation Data for Post-Irradiation Acrylamide Polymer (Sample V)

Fraction	Wt.-% of fractions	$[\eta]$	$\bar{M}_v$
V-1	16.42	1.904	200,000
V-2	16.72	1.561	165,000
V-3	12.99	1.307	137,000
V-4	10.00	1.171	126,000
V-5	17.05	1.090	102,000
V-6	4.86	0.812	89,700
V-7	4.56	0.750	83,600
V-8	5.97	0.574	65,000
V-9	4.56	0.457	52,000
V-10	6.95	0.360	42,000

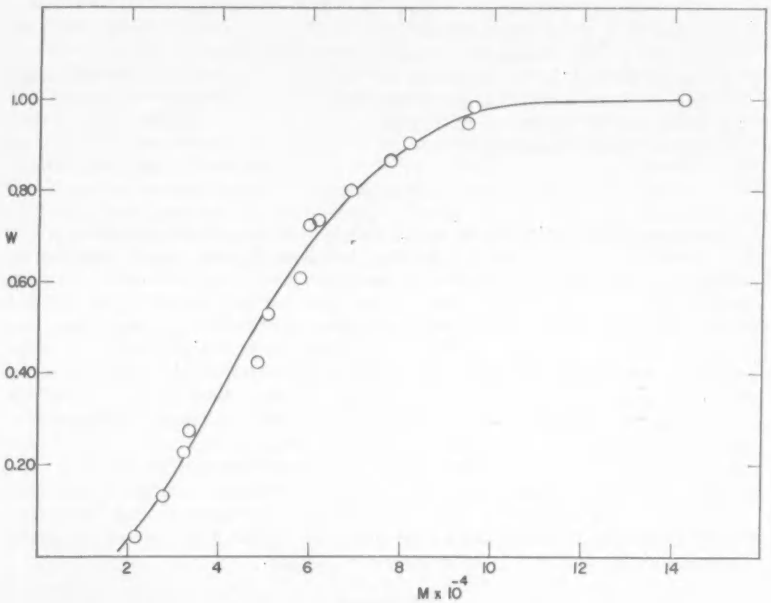

Fig. 2. Cumulative weight distribution for post-irradiation acrylamide polymer: Irradiation dose 0.74 Mrad at −78°C.; post-irradiation storage 26 hr. at 25°C.; conversion 5.8% (sample V).

Morawetz[4] has suggested is out because, if this were true the percentage of constant molecular weight polymer would be higher for the polymer with low (5.8 wt.-%) conversion.

The effect of isomorphous nonpolymerizable material, propionamide, present in solid solution in the acrylamide crystal is very interesting. The over-all rate of polymerization was increased with the presence of propionamide (Table I). This was also observed for in-source polymerization of acrylamide-propionamide system.[1] Very broad molecular weight distribution for acrylamide-propionamide system (sample VI) which can be seen from Table II and Figure 1 indicates that propionamide is not a chain transfer agent, but, even though it is isomorphous with acrylamide, it should introduce more imperfections into crystals.

The author wishes to acknowledge to Dr. D. S. Ballantine, Dr. G. Adler, and Miss A. Glines for preparations of the irradiated polymeric samples.

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11. ASTM Method D-1671-59T.

Synopsis

It has been known for some time that a variety of monomers can be polymerized in the crystalline state by exposure to ionizing radiation. Detailed kinetic studies were published on both the in-source and post-irradiation reactions of acrylamide. Two different approaches were adopted in kinetic interpretations: one was that of conventional polymer chemistry and the other was that of solid-state chemistry. It was claimed that the initial number of chains would be constant throughout the post-irradiation polymerization of crystalline acrylamide and consequently the initial free radical concentration could be calculated from the yield and molecular weight data. It would be difficult to reconcile such a picture with the proposed nucleation mechanism. Consequently, fractionation studies were made on polymer from both in-source and post-irradiation experiments with the hope that the resultant data might further clarify the issue. Preliminary results indicate the occurrence of a significantly large percentage of polymer of constant molecular weight from the post-irradiation experiment is most interesting. Further fractionation data presented in this paper support the proposed nucleation mechanism for the solid-state polymerization of acrylamide.

Résumé

On sait depuis peu de temps que certains monomères peuvent être polymérisés à l'état cristallin par exposition à une radiation ionisante. On a publié des études cinétiques détaillées de réactions in source et de post-irradiation de l'acrylamide. On adopte deux théories différentes pour l'interprétation cinétique: soit celle utilisée par la chimie conventionnelle des polymères, soit celle de la chimie de l'état solide. On a montré que la nombre initial de chaînes reste constant durant la polymérisation par post-irradiation de l'acrylamide cristallin, et par conséquent la concentration initiale en radicaux libres peut être calculée à partir des rendements et des poids radicalaires obtenus. Il semble malaisé de réconcilier un tel schéma avec le mécanisme de nucléation proposé. Des études de fractionnement furent donc entreprises sur le polymère provenant et des expériences in-source et des expériences de post-irradiation en espérant que les résultats puissent ultérieurement solutionner le problème. Les premiers résultats indiquent que la formation d'un pourcentage élevé de polymères de poids moléculaire constant obtenu par post-irradiation est très intéressante. D'autres résultats de fractionnement sont obtenus en fonction du rendement en polymère et pour des polymères préparés à partir de monomères cristallins suivant des techniques préparatories très différentes. Des données supplémentaires de fractionnement présentées dans cet article confirme le mécanisme de nucléation proposé pour la polymérisation de l'acrylamide à l'état solide.

Zusammenfassung

Es ist schon einige Zeit bekannt, dass eine Anzahl von Monomeren durch Einwirkung ionisierender Strahlung im kristallinen Zustand zur Polymerisation gebracht werden kann. Eingehende kinetische Untersuchungen wurden über die Reaktion von Acrylamid während der Bestrahlung und über die Nachreaktion veröffentlicht. Die kinetische Deutung wurde auf zwei Wegen, dem der konventionellen Polymerchemie und dem der Festkörperchemie, versucht. Es wurde behauptet, dass die Zahl der Ketten

während der Nachpolymerisation von kristallinem Acrylamid konstant bleibt und daher die Ausgangskonzentration an freien Radikalen aus Umsatz und Molekulargewicht berechnet werden kann. Es erscheint schwierig, dieses Bild mit dem vorgeschlagenen Keimbildungsmechanismus in Übereinstimmung zu bringen. Zur weiteren Klärung wurden Fraktionierungsversuche an Polymeren aus der Bestrahlungs- und Nachreaktions-phase durchgeführt. Vorläufige Versuche lassen interessanterweise das Auftreten eines recht hohen Anteils an Polymeren mit konstantem Molekulargewicht bei den Nach-Bestrahlungs-Versuchen erkennen. Weitere Fraktionierungsergebnisse sollen an Polymeren bei verschiedenem Umsatz und aus Monomeren, die nach weitgehend verschiedenen Verfahren kristallisiert wurden, gewonnen werden. Weitere hier mitgeteilte Fraktionierungsergebnisse stützen den vorgeschlagenen Keimbildungsmechanismus für die Polymerisation von Acrylamide in fester Phase.

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Radiation-Induced Stereospecific Polymerization of Isocyanate in the Solid State

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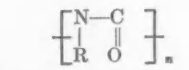
INTRODUCTION

Radiation-induced solid-state polymerizations of several monomers at low temperature were reported from our laboratory.[1] The present paper deals with the radiation-induced polymerizations of isocyanates R—N=C=O in liquid and solid states at low temperature. It was shown by Shashoua et al.[2] that isocyanates polymerize with anionic catalyst at −20 to −100°C. and produce a linear amorphous high polymer having the structure:



Three years ago,[3] we reported the radiation-induced polymerization of isocyanates in both liquid and solid states at low temperature. It was at first found in our experiments that crystalline poly-*n*-butylisocyanate could be obtained by the solid-state polymerization of the monomer.

Very recently, Natta et al.[4] obtained crystalline polymers by polymerizing phenyl- and *n*-butylisocyanate in various solvents in the presence of anionic catalysts such as lithium or sodium alkyls.

It is obvious from both our investigation and Natta's experimental results that the same stereoregular crystalline poly-*n*-butylisocyanate can be obtained, in spite of quite different methods.

EXPERIMENTAL

Methyl-, *n*-butyl-, and phenylisocyanates were used as monomers. These monomers were condensed into an ampule. The ampule containing solid monomer was evacuated to 10^{-2}–10^{-3} mm. Hg. Irradiation was carried out by γ-radiation from Co^{60} source in the temperature range of 20 to −196°C.

Dependencies of irradiation dose, dose rate, and temperature on the polymerization were investigated. The effects of solvent and radical scavenger on the polymerization were also examined.

The infrared spectra of the polymers were measured.

RESULTS AND DISCUSSION

The data conversion versus irradiation dose is given in Figure 1.

The polymerization is not preceded by an induction period.

The effect of dose rate on polymerization of butylisocyanate is shown in Figures 2 and 3.

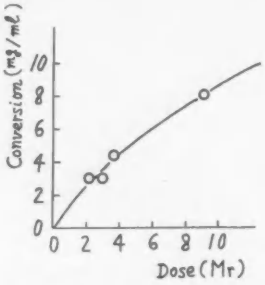


Fig. 1. The relation between conversion and irradiation dose in the radiation-induced liquid-phase polymerization of butylisocyanate at −78°C. Dose rate is 2×10^4 r/hr.

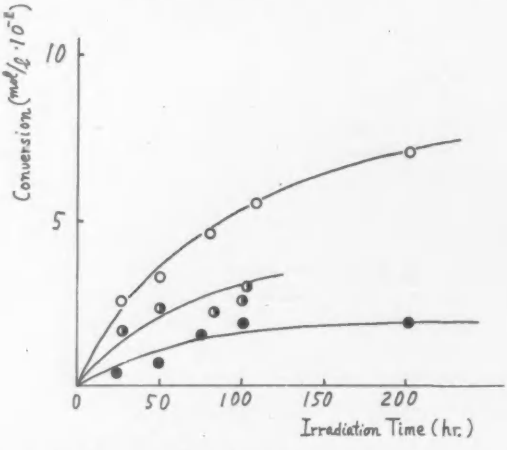


Fig. 2. The effect of dose rate on the polymerization of butyl isocyanate at −78°C. in liquid state of monomer: (●) 2×10^4 r/hr., (◑) 4×10^4 r/hr., (○) 7×10^4 r/hr.

It is apparent from these results that the rate of polymerization is proportional to the dose rate. These results suggest that the termination is a unimolecular process.

1. Temperature Dependence of Polymerization Rate

The effect of temperature on the polymerization is shown in Figure 4 in the case of *n*-butylisocyanate.

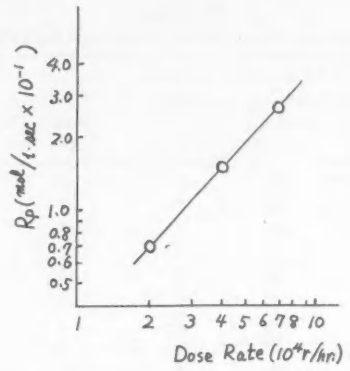


Fig. 3. The relation between logarithmic rate of polymerization and dose rate.

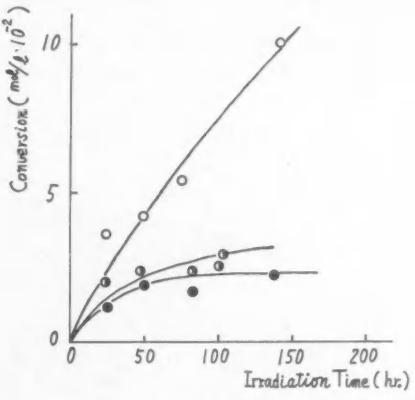


Fig. 4. The effect of temperature on polymerization rate of butylisocyanate: (●) 20°C. (liquid); (◑) −78°C. (liquid); (○) −196°C. (solid).

It is obvious from the figure that polymerization rate is much greater in the solid state than in the liquid state.

In the case of methylisocyanate and phenylisocyanate, the rate of polymerization is almost unchanged in the temperature region of 20 to −78°C.

The apparent activation energy of polymerization of methylisocyanate and *n*-butylisocyanate is very small or slightly negative (about 0 to −0.5 kcal./mole).

2. Polymerization in Dimethylformamide Solution

The effect of solvent on the polymerization was examined. Results are shown in Table I and Figure 5.

TABLE I
Effect of Solvent (Dimethylformamide) on the Polymerization

Monomer	Monomer concentration, vol. %	Dose rate, γ/hr. × 10^4	Dose, Mr	Polymerization temperature, °C.	Yield, %
Methylisocyanate	100	2	4	−78	0.5
Methylisocyanate	50	2	4	−78	1.86
n-Butylisocyanate	100	7	7	18	0.70
n-Butylisocyanate	23	7	7	18	4.26
n-Butylisocyanate	48	7.3	15	−78	1.39
n-Butylisocyanate	23	7.3	15	−78	2.17
Phenylisocyanate	100	2	4	−78	0.47
Phenylisocyanate	55	2	4	−78	28.0
Phenylisocyanate	38	2	4	−78	13.5

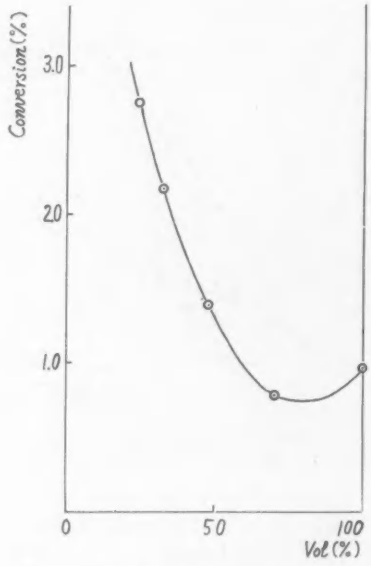


Fig. 5. The effect of solvent (dimethylformamide) on the polymerization.

From these results, it is obvious that the solvent accelerates markedly the rate of polymerization. These facts suggest that the polymerization of isocyanates in liquid phase proceeds by an anionic mechanism.

Effect of DPPH on the Polymerization

The effect of a radical scavenger on the polymerization is shown in Table II.

TABLE II
Effect of Radical Scavenger (DPPH) on the Polymerization

Monomer	Amount of DPPH. mg./cc.	Polymerization temperature, °C.	Dose, Mr	Yield, %
n-Butylisocyanate	0	20	7.0	0.70
n-Butylisocyanate	2.3	18	7.0	0.70
Phenylisocyanate	0	18	7.0	0.70
Phenylisocyanate	2.3	18	7.3	0.70
Phenylisocyanate	0	−78	15.0	0.97
Phenylisocyanate	2.3	−78	15.0	0.48

It is evident from these results that radical scavenger has almost no inhibiting effect on the polymerization. This fact suggests also that the polymerization would proceed by an ionic mechanism.

4. Infrared Spectra of Poly-n-butylisocyanates

The infrared spectra of *n*-butylisocyanates obtained in the liquid-state and solid-state polymerizations are shown in Figures 6 and 7, respectively.

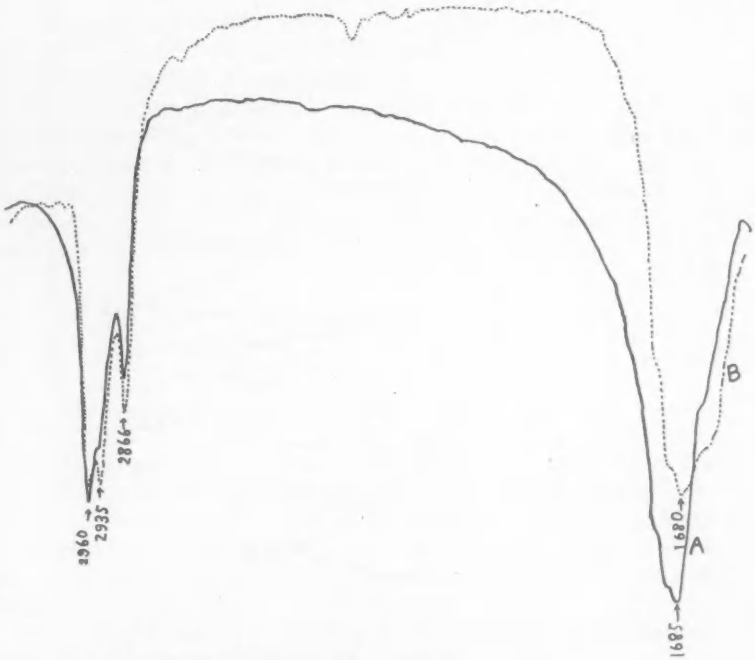


Fig. 6. Infrared spectra of polybutylisocyanate obtained by liquid-phase (*B*) and solid-phase (*A*) polymerization (3000 word −1600 cm.$^{-1}$).

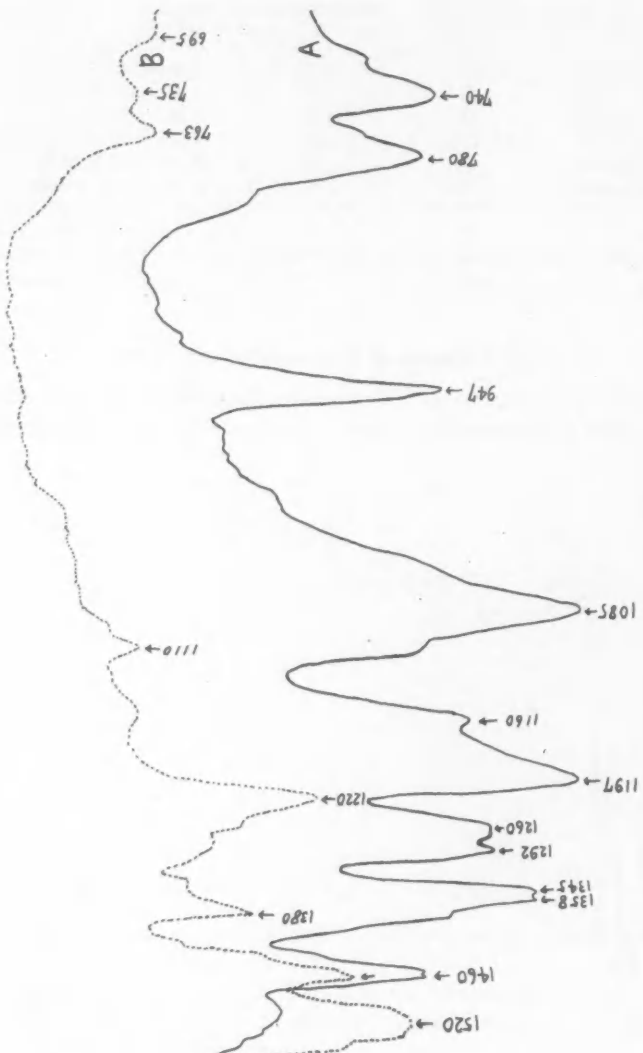


Fig. 7. Infrared spectra of polybutylisocyanate obtained by liquid-phase (*B*) and solid-phase (*A*) polymerization (1550–650 cm. $^{-1}$).

There are marked differences between the spectra of the polymers polymerized in liquid and solid state.

These facts indicate that the structure of polymer chain is very different between both polymers, probably due to the stereo regularity.

Very recently, Natta reported spectrum of a poly-*n*-butylisocyanate prepared by his own method (catalytic liquid-phase polymerization).

The spectrum of poly-*n*-butylisocyanate obtained by radiation-induced solid-state polymerization is quite similar to this one. On the other hand, the spectrum of poly-*n*-butylisocyanate obtained by liquid-state polymerization is very different from both of these spectra.

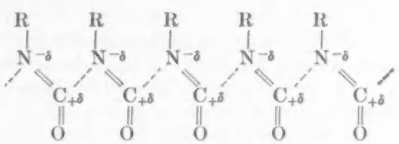
From these experimental results, it is obvious that a stereospecific polymerization is possible for solid-state polymerization at low temperature, as well as in the case of acrylonitrile, methacrylonitrile, acetylene, as already reported.[1,5]

Crystalline poly-*n*-butylisocyanate could not be obtained by liquid-phase polymerization. On the other hand, we could not obtain crystalline polymer from methyl- and phenylisocyanates.

5. Polymerization Mechanism

It is apparent from the results described above that the polymerization in liquid phase proceeds by an anionic mechanism.

On the other hand, the polymerization in the solid state of such monomers at low temperature would proceed by a nonradical mechanism which is nonionic in ordinary sense. We wish to emphasize the importance of the electronic state of the crystal as a whole, in a solid-state polymerization at low temperature. In the case of isocyanate monomer, one can easily postulate the strong electronic interaction between monomers in crystalline state as shown in the following:



It may be easily supposed from such an electronic state of the monomers that the monomer in the crystalline state at low temperature would be in a kind of excited state, due to the strong collective interaction. Therefore, it seems to be not unreasonable to postulate that a long sequence of monomer units would convert instantly to the corresponding high molecular compound by high energy initiation.

The authors proposed a new mechanism, electronic polymerization, for solid-state polymerization at low temperature.[5]

We are now investigating to establish the mechanism by several physical techniques.

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Synopsis

Radiation-induced solid-state polymerizations of isocyanates are reported. It was found that stereospecific polymerization is possible during solid-state polymerization at low temperature. Stereospecific crystalline polymer was obtained from the solid-state polymerization of butyl isocyanate. On the other hand, when the monomer was polymerized in the liquid state, the polymer obtained was amorphous and quite different from that obtained in the solid state. Several other isocyanates were polymerized in both liquid and solid states. Crystalline polymers could not be obtained.

Résumé

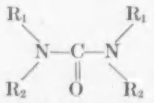
On décrit la polymérisation induite par radiation en phase solide des isocyanates. On a trouvé que la polymérisation stéréospécifique est possible pendant cette polymérisation en phase solide à basse température. Un polymère cristallin stéréospécifique a été obtenu par une polymérisation en phase solide de l'isocyanate de butyle. D'autre part, quand le monomère est polymérisé à l'état liquide, on obtient un polymère amorphe et tout à fait différent de celui obtenu en phase solide. On a polymérisé différents isocyanates en phase liquide et solide. Des polymères cristallins n'ont pas été obtenus.

Zusammenfassung

Es wird die Strahlungspolymerisation von Isocyanaten in festem Zustand beschrieben. Bei der bei tiefer Temperatur durchgeführten Polymerisation in festem Zustand besteht die Möglichkeit zur stereospezifischen Polymerisation. Bei der Polymerisation von Butylisocyanat in festem Zustand entstand ein stereospezifisches kristallines Polymeres. Wurde dagegen das Monomere in flüssigem Zustand polymerisiert, so bildete sich ein amorphes Polymeres, das von dem in festem Zustand erhaltenem deutlich verschieden war. Ausserdem wurden mehrere andere Isocyanate sowohl in flüssigem als auch in festem Zustand polymerisiert. Dabei konnten keine kristallinen Polymeren erhalten werden.

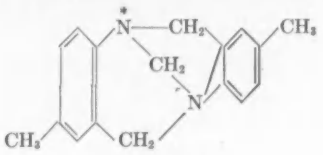
Discussion

H. Morawetz (*Polytechnic Institute, Brooklyn, N. Y.*): It is not clear to me what is meant by stereoregularity in polyisocyanates. This term would be meaningful only if it could be shown that compounds of the type



can exist in a *meso* and a *d,l*-form. Do the authors know of any such case?

Y. Tabata: The question of Prof. Morawetz deals with one of the most important problems in our work. As pointed out by Prof. Morawetz the nitrogen atom is not fixed in the molecule in most cases. But there are some cases in which the atom is fixed in the molecule, depending on the steric hindrance of the molecule. Troeger's Base is one of the typical examples. I would like to quote the following reference (V. Prelog and P. Wieland, *Helv. Chim. Acta.*, **27,** 1127 (1944))



JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 953-965

Production of Polyoxymethylene of High Molecular Weight and High Crystallinity from Trioxane*

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Formaldehyde polymers have been known for many years, but until recently they were considered to be of no practical interest because of their thermal instability (as they tend to decompose to formaldehyde upon heating) and poor mechanical properties. These deficiencies were essentially due to the difficulty of obtaining products of sufficiently high molecular weight, but more recently, thanks to intensive research in this field, formaldehyde polymers of very high molecular weight and sufficient thermal stability (which can be improved by successive chemical treatments) have been produced and are now becoming commercially available. These new materials, characterized by very good mechanical properties, high distortion temperature, high solvent resistance, and excellent dielectric properties, are of relatively low cost and are considered of a commercial potentiality competitive with that of polyolefins. The starting materials used in the preparation of the high molecular weight polyoxymethylenes are essentially formaldehyde and trioxane. The latter has the advantage over the former of being more easily purifiable and manipulated. As early as 1922 Hammick and Boeree[1] and in 1932 Kohlschutter and Sprenger[2] demonstrated that trioxane could be easily polymerized to give high molecular weight products by simple sublimation under vacuum through a typical topochemical reaction. A polyoxymethylene of high melting point (195–200°C.) could be obtained in this way. Only a few years ago, after the commercial introduction on the market of du Pont's Delrin resins, intensive investigation in the field of the polymerization of trioxane was begun, most of the studies being carried out at the laboratories of the Celanese Corporation.

The polymerization of trioxane can be carried out in solution of different solvents (oxygenated, chlorinated, or pure hydrocarbons, especially cyclohexane), in suspension, or in "mixed" systems (i.e., partly in solution, partly in suspension), making use of media with varying solvent power for trioxane (generally hydrocarbons of various molecular weights[3]).

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A broad range of active initiators can be used for the polymerization of trioxane. These are, in general, by metal halides, particularly boron trifluoride, their complexes with ethers or oxonium or diazonium salts, boric acid trisamides, amines, imides, quaternary ammonium compounds, carbinamides and thiocarbonamides, phosphines, arsines, stibines, sulfur compounds, mineral acids, organic acids, metalloorganic compounds, etc.

In general, the polymerization in solution of both trioxane and formaldehyde leads to polymers of low molecular weight and low degree of crystallinity.

To the contrary, in products obtained through topochemical polymerization of trioxane in heterogeneous gas–solid phase by sublimation of the monomer on the polymer, or in heterogeneous liquid–solid phase in which the liquid phase consists of aqueous formaldehyde solution, the degree of crystallinity is very high.[4]

Japanese authors[5] have carried out the polymerization of trioxane to polyoxymethylene with a high molecular weight and a high melting point, by subjecting the monomer to γ-irradiation or by electron bombardment of single crystals of trioxane; an analogous phenomenon has been observed with other cyclic crystalline monomers (diketene, β-propiolactone, 3-3 bischloromethylcycloxybutane).

It is, however, evident that the application of these methods on a industrial scale involves special difficulties. Moreover, it must be kept in mind that in the polymerization induced by high energy radiations, these may lead to the destruction of crystallites of the polymer, to the formation of crosslinks between chains, or to degradation of the chains. All these changes modify more or less profoundly the structure of the material and, consequently, its properties.

We tried to carry out the polymerization of trioxane from crystalline seeds of this substance, activated by a suitable catalyst. Our choice fell on those catalysts which proved to be effective in the polymerization of formaldehyde in the aqueous phase (in particular Lewis acids and their complexes).

It was foreseen and successively confirmed by experimental results that, to obtain highly crystalline polymers from trioxane in good yield, it was necessary to provoke a gradual, continuous crystallization of the monomer in the form of small single crystals of suitable dimensions, in order to avoid formation of aggregates, which would disturb the course of the polymerization. This may be achieved in a simple way by favoring the crystallization of trioxane from a solution in an appropriate solvent through a gradual lowering of temperature.

In any case, it is necessary that the rates of formation of crystalline seeds and of their subsequent growth be kept within appropriate limits to obtain the optimal conditions for polymerization which may follow immediately, namely, they must be no higher than the rate of polymerization.

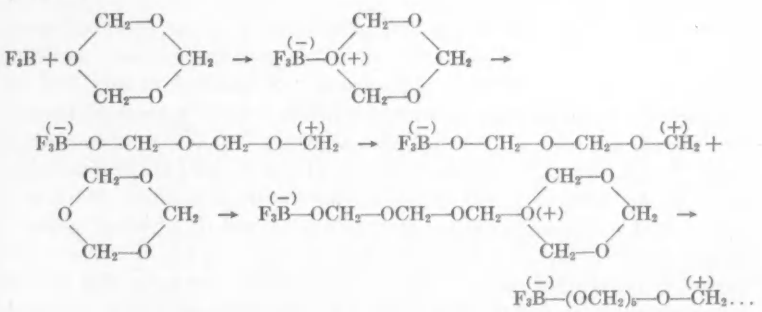
The solvent must be chosen with particular care, especially with regard to its polarity, which may influence the course of the ionic polymerization,

its viscosity, which may influence the rate of crystallization and the formation of polycrystalline aggregates (which, as above stated, is to be avoided) and, finally, its solvent power with respect to the catalyst. It may be foreseen that the viscosity of the medium must be the higher, the lower the rate of polymerization and, other conditions being equal, the lower the concentration of the catalyst. This in order to prevent the rate of crystallization from being greater than that of polymerization.

Also, stirring of the reaction mixture during the crystallization-polymerization process must be controlled. Very vigorous agitation may favor particularly the rate of crystalline nucleation and formation of polycrystalline aggregates, thus disturbing the phenomenon. In general, it may be foreseen that agitation is to be limited just to the minimum necessary to assure macroscopic homogeneity of the system, heat removal, and temperature regulation.

If the crystallization of trioxane is brought about by decreasing the temperature, it is necessary to regulate the latter phenomenon and the consequent oversaturation of the solution, taking first of all into account the influence that it exerts on the rates of formation of nuclei and of their subsequent growth, and moreover the influence of temperature on these phenomena and on the rate of polymerization.

It has been found that if a cationic catalyst is employed, the polymerization of trioxane is characterized by an induction period, during which no high molecular products but only formaldehyde and its oligomers are formed. With the use of cationic catalyst such as BF_3, according to Kern and Jaacks,[6] formation of oligomers occurs which is activated as shown in the scheme:



These oligomers which tend to grow by addition and opening of rings, at the same time partly decompose to give free formaldehyde. Only when a given equilibrium concentration of formaldehyde is established, do polymers begin to form. In effect, the induction period tends to disappear if, before addition of the catalyst, a quantity of free formaldehyde, corresponding to the equilibrium concentration, is added. In presence of formaldehyde, formation of activated oligomers may also occur by reaction of formaldehyde with catalyst.

EXPERIMENTAL AND RESULTS

Materials and Apparatus

Experiments were carried out by dissolving trioxane at temperatures above its melting point (61–62°C.) in various solvents with different characteristics (density, viscosity, solvent power, dielectric constant, etc.) and letting the solution to cool to room temperatures or lower at a controlled constant rate in order to favor gradual precipitation of trioxane in the form of small single crystals. Our solvent of choice, after these preliminary experiments, was vaseline oil, whose viscosity is sufficiently high (about 50–200 epoises at 20°C., depending on the density) and which, while dissolves trioxane up to about 10% at 61–62°C., favors its nearly complete precipitation from the solution by cooling to room temperature. The precipitate consists of needlelike small crystals of trioxane, which gradually appear from the solution upon cooling and remain well suspended in the mass, well separated from one another without exhibiting any tendency to agglomerate or to settle at the bottom of the reaction vessel.

After the choice of the solvent, experiments were carried out in order to induce polymerization of the trioxane crystals during their formation. The experimental apparatus consisted of a cylindrical glass vessel (furnished with cooling coils and an agitator), closed by a stopcock with three sockets carrying the thermometer and the catalyst and monomer inlets. The whole apparatus is kept in a thermostat with a liquid circulation pump connected to the coils inside the vessel.

Procedure

The solvent (vaseline oil) is first introduced into the reaction vessel, located in the thermostat kept at the initial temperature (above the melting point of trioxane 61–62°C.). The amount of purified molten trioxane required to obtain a nearly saturated solution is then introduced through the appropriate inlet. After vigorous agitation to allow solubilization of most of the trioxane, the catalyst is added (BF_3 etherate) in small amounts, after having been dispersed at room temperature in a small quantity of vaseline oil. When all the catalyst has been added, agitation either is regulated at constant speed or completely stopped and the mixture allowed to cool at a controlled rate to a definite final temperature (generally to room temperature). As the temperature of the reaction mass drops, formation of long fibers, whose quantity gradually increases with decreasing temperature, is observed. The fibers remain well dispersed in the reaction medium, without depositing at the bottom of the vessel, and gradually thicken the reaction mixture which, when temperature is of the order of 40–30°C., assumes a gellike consistency. At the end of the reaction, when the mixture has reached the final temperature, the gelatinous mass is extracted from the vessel, centrifugated to eliminate most of the majority of vaseline oil and, successively, washed with gasoline or petroleum ether.

The reaction product is composed of a mixture of a fiberlike substance together with a minor amount of a powdery product, both consisting of polyoxymethylene with high molecular weight.

The fiberlike product melts at 186–187°C. and exhibits an inherent viscosity (determined in *p*-chlorophenol for $c = 0.5\%$ at 60°C.) of 1.1–2.0. X-ray examination shows a degree of crystallinity of the order of 97–98%, and orientation of crystallites in the direction of the *c*-axis (axis of the fiber and of the polymer chain). The fibers show good thermal stability and good film-forming properties, even in the unstabilized state.

On the other hand, the powdery product melts at lower temperature (178–180°C.), exhibits lower inherent viscosity (about 0.7–1.1) and lower thermal stability as compared with the fibers, with poor or no film-forming properties in the unstabilized state. X-ray examination shows a crystallinity of the order of 90%, without any preferred orientation of crystallites.

The yields of the reaction and the fibers/powder ratio vary very much depending on: (*a*) rate of stirring, (*b*) rate of cooling, (*c*) concentration of initial solution, (*d*) viscosity of the solvent, (*e*) initial and final temperatures, (*f*) catalyst concentration.

The effect of each single factor will be separately described.

1. Effect of Stirring. Figures 1 and 2 show total yields and per cent fibers, respectively, as functions of rate of stirring on a logarithmic scale relative to experiments carried out in substantially similar general conditions, only the rate of stirring being varied. These experiments were performed by preparing practically saturated solutions of trioxane in vaseline oil (about 10%) (viscosity at 20°C. = 109 cpoises) at temperatures just above the melting point of trioxane (61–62°C.) with vigorous agitation and then, adding dropwise a certain quantity of catalyst (0.8 ml./g.) of monomer suspended in a small amount of vaseline oil. When all the catalyst had been added, agitation was continued, or reduced, or com-

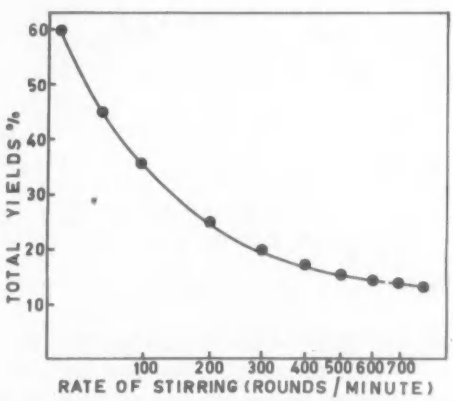


Fig. 1. Total yield of polyoxymethylene as a function of rate of stirring.

pletely stopped and the reaction mass allowed to cool from the initial to room temperature at a controlled rate (20°C./hr.).

The results graphically reported in Figure 1 show that when vigorous stirring is maintained during the whole course of the reaction, total yields

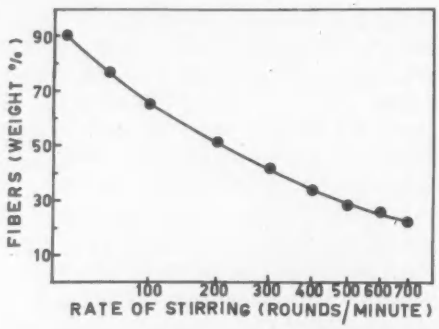


Fig. 2. Per cent fibers in the polymer as a function of rate of stirring.

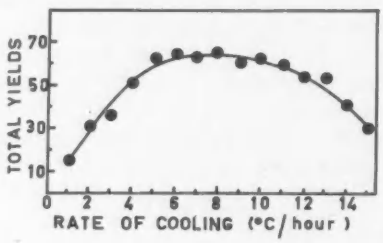


Fig. 3. Total yield of polyoxymethylene as a function of the rate of cooling.

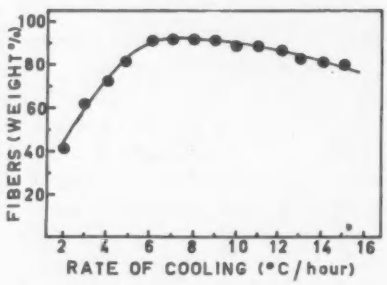


Fig. 4. Per cent fibers in the polymer as a function of the rate of cooling.

and fiber yields are low. On the contrary, when the rate of stirring is reduced to a few revolutions per minute total yield increases and fibers in large proportion as compared to the powdery product are formed. The relative abundance of the latter increases with increasing rate of stirring.

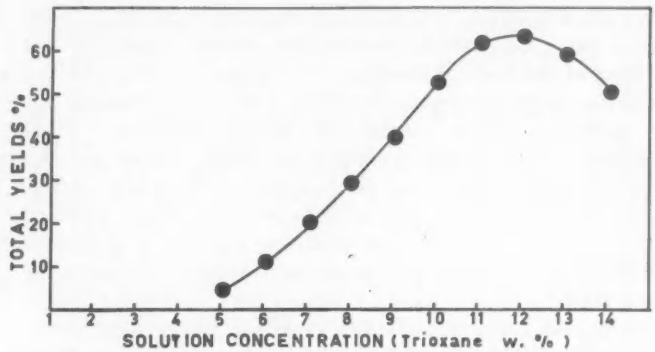


Fig. 5. Total yield of polyoxymethylene as a function of the trioxane/solvent ratio.

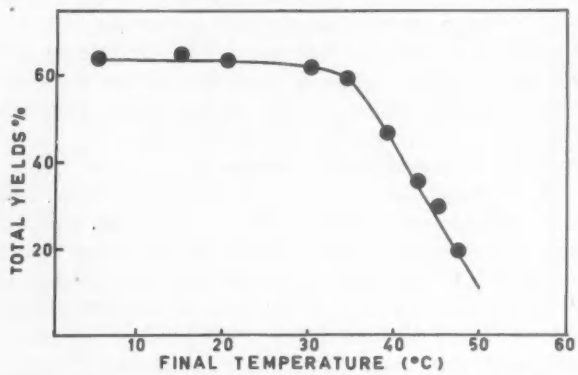


Fig. 6. Total yield of polyoxymethylene as a function of the final temperature.

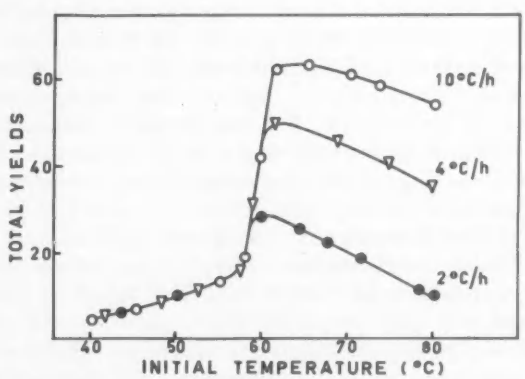


Fig. 7. Total yield of polyoxymethylene as a function of the initial temperature at various cooling rates.

Finally, when agitation is completely stopped, total yields reach their maximum value and most of the polymeric product consists of fibers.

2. Effect of the Rate of Cooling. In Figures 3 and 4 total yields and per cent fibers are reported as functions of the rate of cooling, for experiments carried out under substantially similar conditions. In all these experiments, to an initial practically saturated solution of trioxane in vaseline oil, kept at 62°C., a certain quantity of catalyst 0.8 ml./g. of monomer (BF_3 etherate) was added, dropwise, while stirring. After addition of all the catalyst, agitation was completely stopped and the reaction mass allowed to cool from initial to room temperature (20°C.) at different rates.

From the data reported in Figures 3 and 4, it can be observed that, with very low cooling rates (about 4°C./hr), low total yields are obtained with a high proportion of powder over fibers. With increasing rate of cooling, total yields increase, pass through a maximum for cooling rates of the order of 6–13°C./hr., and, successively, tend to decrease with further increase of the rate of temperature decrease. The fiber powder ratio, however, which, as previously stated, is quite low for low rates of cooling, increases with increasing rate of cooling, tending toward a value which is practically constant for high rates of temperature drop.

3. Effect of the Monomer/Solvent Ratio. In Figure 5 total yields are reported as functions of the monomer/solvent ratio. These experiments were carried out under substantially similar conditions, only the initial concentration of the monomer being varied. As can be seen from the data reported in Figure 5, total yields are very low when very dilute solutions of trioxane in vaseline oil are used; they tend to increase with increasing monomer/solvent ratio, reaching their maximum values for concentrations very near the saturation point at the initial temperature (62°C.).

In these experiments, it was noted that, if the initial solution is prepared in such a way as to leave a small quantity of molten trioxane in the undissolved state at the initial temperature, polymerization starts as soon as the catalyst is added. However, when all the trioxane used goes completely into solution at the initial temperature, a certain induction period is observed and the polymerization fails to occur if cooling is started soon after addition of the catalyst. For this reason, in all experiments here described, when, carried out in the absence of molten unsolved trioxane, the initial mixture was kept for several minutes at the initial temperature used to initiate the process before cooling.

4. Effect of Final Temperature. In Figure 6 total yields are reported as functions of the final temperature. The experiments here have all been performed under substantially similar conditions, only the final temperature being changed.

From the data reported in Figure 6, it can be seen that the total yields are higher, the lower the final temperature. For final temperatures of 10–25°C., yields are practically constant; for final temperatures above 25°C., on the contrary, a lowering of yields occurs. This is gradual when

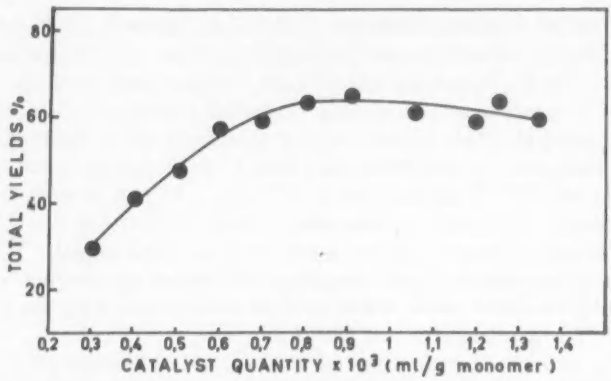


Fig. 8. Total yield of polyoxymethylene as a function of amount of catalyst.

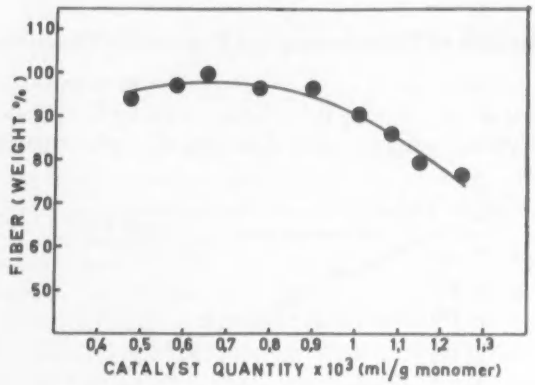


Fig. 9. Per cent fibers in the polymer as a function of catalyst concentration.

the final temperatures are between 25 and 35°C. and becomes very steep for final temperatures above 35°C.

5. Effect of Initial Temperature. In Figure 7 total yields are reported for experiments in which the effect of the changes in the initial temperature was investigated, all other condition remaining fixed.

In these experiments, nearly saturated solutions of trioxane in vaseline oil were prepared at 62°C.; successively, they were warmed or cooled to a definite initial temperature and, after addition of the catalyst, left to cool to room temperature at different rates without agitation.

When initial temperatures below 60°C. are used, very low yields are obtained, in any case. With initial temperatures just above 60°C., maximum yields are obtained. Finally, at still higher temperatures, yields tend to decrease with increasing initial temperature. This effect is more marked in experiments in which lower rates of cooling are employed.

6. Effect of Catalyst/Monomer Ratio. In Figure 8 total yields are reported as function of the catalyst/monomer ratio. The data reported in this figure are for experiments carried out in almost saturated solutions of trioxane in vaseline oil, in absence of molten trioxane.* The solutions were prepared at 62°C., allowed to stand 20 min. at the initial temperature for initiating the polymerization and then cooled from the initial to room temperature (20°C.) at the rate of 20°C./hr. As can be seen from the data reported in Figure 8, when quantities of catalyst below 2.5×10^{-4} ml./g. of monomer are used, no polymerization occurs at all. When the catalyst concentration is increased, total yields increase tending toward a practically constant value when catalyst concentration of the order of 1×10^{-3} ml./g. of monomer are reached.

In Figure 9, the fibers/powder ratio is reported as function of concentration of catalyst. As it can be seen from the curves reported in the Figure 9, the fiber/powder ratio steadily decreases with increasing concentration of catalyst.

Thermal Stability of Polyoxymethylene Obtained by Described Method

For the determination of the thermal stability of polyoxymethylene an apparatus was set up following the technique used by Naylor and Anderson for other polymers.[7] This consists in heating a polymer sample in a glass

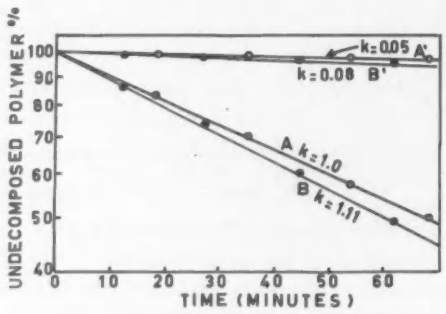


Fig. 10. Thermal stability data at 222°C.

bulb open to the atmosphere through a capillary tip, the bulb being suspended from the arm of a sensitive balance and into a vapor bath or an air thermostat.

By this method, following the loss in weight of a polymer sample (about 0.5 g.) as function of time, at constant temperature, the rate of thermal

* Although in normal practice it is more desirable to start with nearly saturated solutions in presence of small quantities of molten trioxane, in these experiments, in which the effect of catalyst concentration is evaluated, it was preferred to avoid presence of molten trioxane in the initial mixture, which, while it supresses the induction period, may destroy a certain quantity of catalyst, so the effect of its concentration on yields cannot be well estimated.

decomposition can be determined at the given temperature. The thermal decomposition of polyoxymethylenes has been proved to be a first-order reaction and hence, by plotting the log of the weight per cent U of the material undecomposed versus time, straight lines are obtained, from the slopes of which the rate constant K can be calculated. The temperature of 222°C. was chosen, as generally the stability data of polyoxymethylene reported in literature are referred to this temperature.

In Figure 10 log U is reported as a function of time at the temperature of 222°C., as determined in a typical fiberlike polymer, prepared by our method, before and after stabilization. The calculated K_{222} values are reported in Table I.

TABLE I
Thermal Stability Data for Fiberlike Polyoxymethylene

Sample	K_{222}
A	1.0
A′ (stabilized)	0.05
B	1.11
B′ (stabilized)	0.08

The stabilization of the fibers was accomplished by esterification with acetic anhydride in presence of small quantities (0.001–0.1 g./100 ml. of acetic anhydride) of sodium acetate at 180°C. under pressure in a Carius tube.

At lower temperatures, unlike what happens for the powdery polyoxymethylene which readily dissolves and reacts with boiling acetic anhydride at normal pressure (132°C.), very poor esterification of fibers is obtained, as these are hardly attacked by the solvent due to the close arrangements of polymeric chains.

As it can be seen from the data reported in Figure 10, K_{222} of the order of 1.0–1.1 can be obtained for the unstabilized polymer, which is indicative of good thermal stability of the product. Values are in the range of 0.05–0.08 for the stabilized polymer.

Dynamic Mechanical Properties of Polyoxymethylenes

In Figure 11, the dynamic mechanical properties (sound velocity and damping factor Q^{-1}), determined in two stabilized samples of polyoxymethylene by us prepared by melting the fibers (A) for different temperatures are compared with those relative to a sample of Delrin (B) measurements have been made by an electrostatic method at frequencies of the order of 10^4 Hz.

From the values of the sound velocity v in grams/cm.^{3} and of the density d, in centimeters/sec., Young's modulus E in dynes/cm.^{2} can be calculated by means of the relation:

$$E = dv^2$$

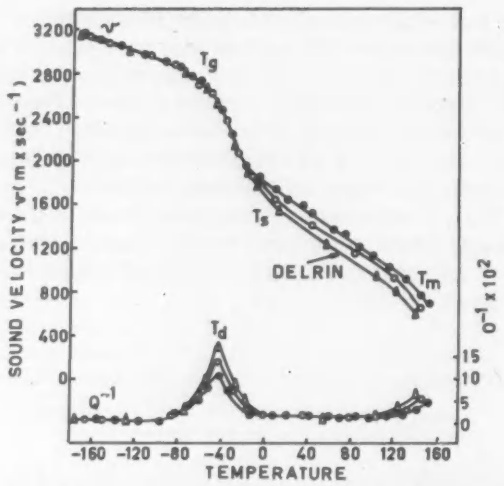


Fig. 11. Sound velocity v and damping factor Q^{-1} in polyoxymethylene.

As can be observed from the data reported in Figure 11, the mechanical spectrum of the samples prepared by us is similar to that shown by Delrin. At temperatures below T_g the values of the sound velocity and the damping factor are practically coincident for the three samples; at temperature above T_g higher values for v and lower for Q^{-1} (in the region of high dissipation) are found for the samples by us prepared, due to their higher crystallinity as compared to Delrin.

CONCLUSIONS

The above reported results indicate that starting from solutions of trioxane in viscous hydrocarbons, in presence of small amounts of a cationic catalyst (BF_3 etherate), it is possible to obtain with high yields, polyoxymethylene with high molecular weight and high crystallinity in closely packed and oriented fiberlike aggregates.

These results can be achieved by provoking polymerization of trioxane during crystallization from a saturated solution in hydrocarbon of determined viscosity and viscosity index trough a gradual controlled lowering of temperature. This process seems to consist in the polymerization of trioxane through growth of activated oligomeric seeds.

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Synopsis

A method is described for the preparation of polyoxymethylene of high molecular weight and high crystallinity in the form of small fibers oriented along the *c* axis of chains, through polymerization of trioxane. It consists in preparing, at temperatures higher than the melting point of trioxane (63–64°C.), almost saturated solutions of trioxane in hydrocarbons of high viscosity, which, after addition of a cationic catalyst (BF_3 etherate), are cooled to room temperature at a controlled rate, without stirring. Trioxane, which precipitates from the solution during the cooling period, polymerizes during crystallization, forming fibers of polyoxymethylene of high molecular weight. The product melts at 186–187°C. and is characterized by inherent viscosities of the order of 1.1–2.0 in *p*-chlorophenol (0.5%) at 60°C. The influences of various factors: rate of stirring, rate of cooling, catalyst concentration, and final and initial temperatures, are described.

Résumé

On décrit une méthode de préparation de polyoxyméthylène de haut poids moléculaire et de cristallinité élevée sous forme de courtes fibres orientées le long de l'axe *c* chaînes, au moyen de la polymérisation du trioxane. Pour ce faire on prépare à des températures plus élevées que le point de fusion du trioxane (62–64°C), des solutions pratiquement saturées de trioxane dans des hydrocarbures de viscosité élevée. Ces solutions, après addition d'un catalyseur cationique (BF_3-éthérate), sont refroidies à température de chambre suivant une vitesse contrôlée et sans agitation. Le trioxane qui précipite de la solution pendant la période de refroidissement polymérise lors de la cristallisation en formant des fibres de polyoxyméthylène de poids moléculaire élevé. Le produit fond à 186–187°C et se caractérise par une viscosité propre de l'ordre de 1.1–2.0 en solution dans le *p*-chlorophénol (0.5%) à 60°C. On décrit l'influence de différents facteurs: vitesse d'agitation, vitesse de refroidissement, concentration en catalyseur, températures initiales et finales.

Zusammenfassung

Eine Methode zur Darstellung von hochmolekularen und hochgradig kristallinem Polyoxymethylen in Form kleiner, längs der *c*-Achse der Ketten orientierten Fasern durch Polymerisation von Trioxan wird beschrieben. Sie besteht in der Bereitung von praktisch an Trioxan gesättigten Lösungen in hochviskosen Kohlenwasserstoffen bei Temperaturen oberhalb des Schmelzpunktes von Trioxan (62–64°C), welche nach Zusatz eines kationischen Katalysators (BF_3-Ätherat), mit geregelter Geschwindigkeit ohne Rühren auf Raumtemperatur abgekühlt werden. Trioxan, das während der Abkühlung aus der Lösung ausfällt, polymerisiert im Augenblick der Kristallisation und bildet hochmolekulare Polyoxymethylenfasern. Das Produkt schmilzt bei 186–187°C und wird durch eine Viskositätszahl in der Grössenordnung von 1,1–2,0 in *p*-Chlorphenol (0,5%) bei 60°C charakterisiert. Der Einfluss verschiedener Faktoren, wie: Rührgeschwindigkeit, Abkühlungsgeschwindigkeit, Katalysatorkonzentration, Anfangs- und Endtemperatur wird beschrieben.

POLYMERIZATION UNDER UNUSUAL CONDITIONS AND WITH NEW CATALYSTS

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La Cinétique de la Polymérisation Vinylique avec des Persels en Milieu Non Aqueux

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I. INTRODUCTION

Le comportement des persels, de type perchlorates anhydres, dans la polymérisation des monomères vinyliques est très peu connu.

Lilley et Foster[1] ont constaté que le perchlorate de magnesium peut déterminer la polymérisation du styrène en phase hétérogène.

Eley et Richards[2] considèrent que l'activité catalytique présentée par le perchlorate d'argent lors de la polymérisation de l'ether vinyl-octylique est due à l'action cocatalytique des traces d'eau.

Losev et Zakharova,[3] analysant les données obtenues dans la polymérisation du styrène avec les perchlorates de potassium, d'ammonium, de barium ou de magnésium à des températures situées entre 20 et 90°C, pendant 8 heures, considèrent que le mécanisme de cette polymérisation est de nature ionique et que l'initiation aurait lieu à la surface des particules de perchlorate, la croissance de la chaîne s'effectuant dans la masse du monomère.

Les protons nécessaires à l'initiation résulteraient, dans ce cas, de l'acide perchlorique adsorbé à la surface des perchlorates ou des traces d'eau existant dans ces derniers. En essayant de polymériser un grand nombre de monomères vinyliques à l'aide des perchlorates de lithium, d'ammonium ou de magnésium anhydre, toujours en phase hétérogène, Hodgon[4] arrive à la conclusion que tous les perchlorates ne sont pas des catalyseurs efficaces et surtout qu' un grand nombre de monomères vinyliques ne peut être polymérisé avec ces types de catalyseurs.

Ce même auteur propose un mécanisme basé sur la capacité de coordination de l'ion de lithium, en vue d'expliquer le mécanisme de polymérisation avec le perchlorate de lithium anhydre.

Il est probable que si l'on avait travaillé en phase homogène, beaucoup des monomères dont Hodgon a affirmé qu'ils ne polymérisaient pas avec les perchlorates de lithium ou de magnésium, même à 80°C, tels que le *N*-vinylcarbazole par exemple, auraient tout de même polymérisé.

Afin de vérifier cette hypothèse, nous avons essayé, dans nos laboratoires, de créer des conditions qui permettent la dissolution simultanée du monomère et du perchlorate, c'est à dire le déroulement de la réaction en phase

homogène, en tenant compte de la capacité de solvation du contre-ion et de la valeur de la constante diélectrique du solvant.

Les persels se sont révélés, dans ce cas, être des catalyseurs extraordinairement actifs pour la polymérisation des monomères ayant une grande densité d'électrons π à la double liaison vinylique. Ainsi, dans des solvants tels que l'acétate d'éthyle, l'acétate d'amyle, l'acétone et le nitrobenzène, le *N*-vinylcarbazole polymérise rapidement en présence de perchlorate de magnésium.

II. PARTIE EXPERIMENTALE

En utilisant la méthode dilatométrique pour étudier la cinétique de réaction de la polymérisation du *N*-vinylcarbazole dans l'acétate d'éthyle, en présence de perchlorate de magnésium, on a réussi à obtenir des données parfaitement reproductibles.

L'introduction des réactifs liquides s'effectue à l'aide d'une seringue hypodermique. Si l'on opère rapidement, il n'est pas nécessaire d'utiliser une "boite sèche" car la polymérisation n'est pas gênée par l'oxygène ou l'humidité atmosphériques.

Le dilatomètre et les récipients de réactifs sont séchés à 110°C, de 10 à 12 heures, puis refroidis dans des récipients séchés à l'aide d'anhydrisants solides.

L'acétate d'éthyle, de provenance Fluka, est lavé avec une solution à 10% de Na_2CO_3, séché sur $CaCl_2$ pendant 24 à 48 heures et ensuite il est distillé sur une colonne Braun. La fraction avec laquelle on travaillait se caractérisait par P_{Eb} (760 mm): 77,1–77,2°C.

Avant chaque polymérisation, l'acétate est redistillé.

Le perchlorate de magnésium, d'origine Merck, est utilisé à l'état de solution à 9,5% dans l'acétate d'éthyle. La concentration de la solution est verifiée par dosage du magnésium.

Le *N*-vinylcarbazole avait une pureté de 99,99% et un point de fusion de 64,50°C.

Le dosage des traces d'eau dans les réactifs est effectué selon la méthode Fischer.

Les expériences de polymérisation ont eu lieu à 20, 25, 30, 35 et 40°C.

Les concentrations de monomère utilisées étaient de 1,25 mole/l et celles des catalyseurs de 0,8 à 5,0 $\times 10^{-3}$ mole/l. Les solutions de catalyseur, de même que celles du monomère dans le solvant, sont limpides. Si l'on assure une parfaite étanchéité des récipients de conservation, la solution de perchlorate de magnésium dans l'acétate d'éthyle ne perd pas son activité pendant deux semaines à 25°C.

La réaction de polymérisation se déroule en milieu homogène jusqu'à un taux de conversion de 30 à 40%, après quoi il apparait une opalescence du milieu de polymérisation due à la précipitation du polyvinylcarbazole insoluble dans l'acétate d'éthyle.

La préparation des polymères en vue d'effectuer les déterminations des masses moléculaires et du rendement est réalisée selon les méthodes utilisées dans d'autres travaux.[5]

III. RÉSULTATS EXPÉRIMENTAUX

A. Rapidité de la Réaction

La réaction de polymérisation en bloc du *N*-vinylcarbazole, à 65°C avec le $(ClO_4)_2Mg$, en solution est violente et même explosive, même pour de très faibles quantités de catalyseur utilisées. La polymérisation s'effectue avec un grand dégagement de chaleur et on observe l'apparition d'une coloration intense rouge-marron qui marque l'apparition du carbocation de *N*-vinylcarbazole dans le milieu réactionnel.

Le processus de polymérisation en solution d'acétate d'éthyle du *N*-vinylcarbazole avec le $(ClO_4)_2Mg$ se déroule de façon plus tempérée et peut être étudié assez facilement par dilatométrie. Pour des concentrations peu élevées de monomère et de catalyseur, la reproductibilité est assurée et on constate, dans ce cas aussi, l'apparition de la coloration rouge-marron au moment de l'addition de la solution de catalyseurs à la solution de monomère.

Le processus de polymérisation est complètement inhibé par les bases organiques fortes et par l'eau.

B. Deroulement de la Polymerisation du *N*-Vinylcarbazole a l'Aide du $(ClO_4)_2Mg$ dans l'Acetate d'Ethyle

Le mode de polymérisation du *N*-vinylcarbazole en fonction du temps, pour diverses concentrations de catalyseurs $[C_0]$ à la température de 30°C, et pour une concentration en monomère de $[M_0] = 1{,}25$ mole/1 est indiqué sur la Figure 1.

Comme il ressort des diagrammes de la Figure 1, le taux de conversion est influencé par l'augmentation des concentrations de catalyseurs et présente une proportionnalité en fonction du temps pour un certain domaine où la dépendance est linéaire.

Dans des intervalles de temps relativement courts, on peut obtenir des rendements jusqu'à 90%.

C. Vitesse de Reaction

Les résultats montrant la dépendance de la vitesse de réaction en fonction de la concentration du catalyseur sont donnés sur la Figure 2. Comme il résulte du diagramme présenté sur la Figure 2, la vitesse de réaction est proportionnelle à la concentration du catalyseur et prend des valeurs élevées pour des concentrations de l'ordre de 3 à 5×10^{-3} mole/1.

L'étude de la vitesse initiale à l'aide de la méthode dilatométrique nous a permis d'observer, dans ce cas, l'existence d'un processus principal de polymérisation du premier ordre, soit en rapport avec la concentration de

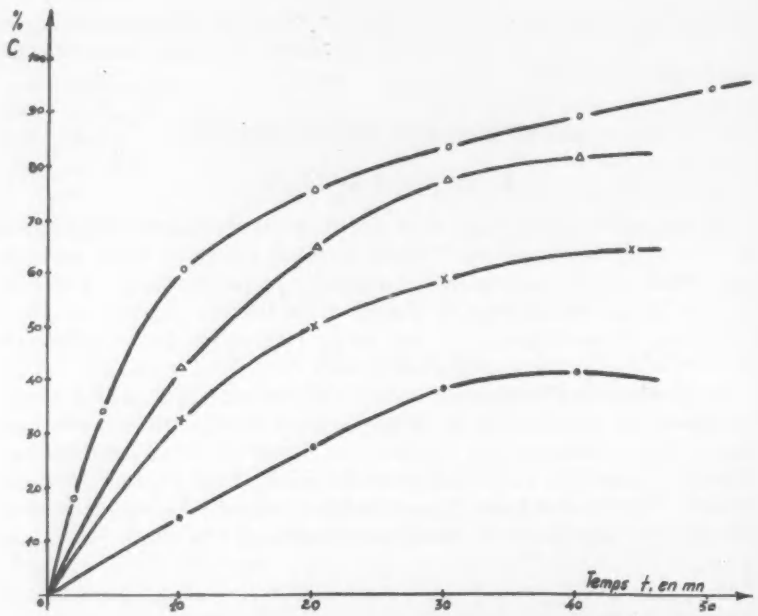

Fig. 1. Courbes de polymérisation du *N*-vinylcarbazole initiée par le perclorate de magnésiun dans l'acétate d'éthyle à 30°C, $[M_0] = 1{,}25$ mole/1: (O) $[C_0] = 0{,}8 \times 10^{-3}$ mole/1; (×) $[C_0] = 1{,}6 \times 10^{-3}$ mole/1; (Δ) $[C_0] = 3{,}2 \times 10^{-3}$ mole/1; (□) $[C_0] = 4{,}8 \times 10^{-3}$ mole/1.

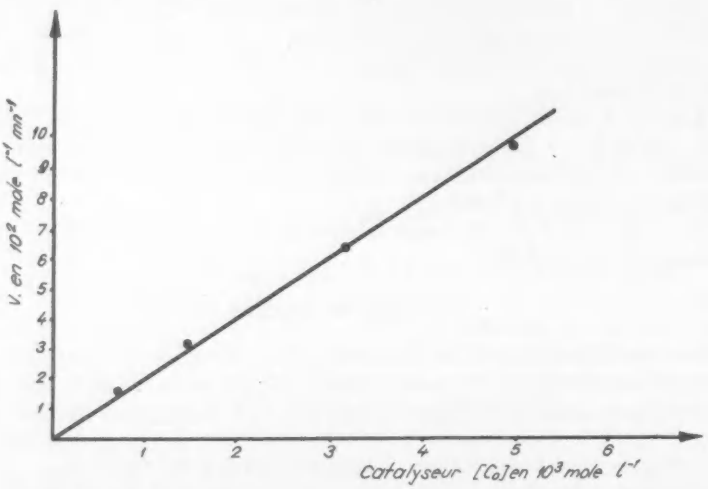

Fig. 2. Etude de la vitesse de polymérisation du *N*-vinylcarbazole a $[M_0] = 1{,}25$ mole/1 en fonction des concentrations initiales du catalyseur $(ClO)_4)_2Mg$.

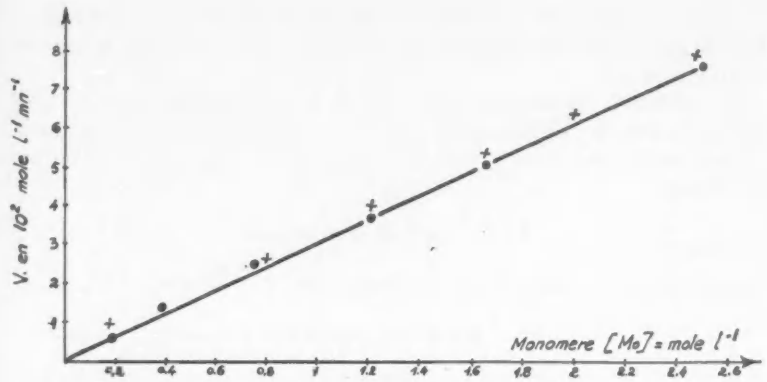

Fig. 3. Etude de la vitesse de polymérisation du *N*-vinylcarbazole en fonction des concentrations initiales en monomère pour une concentration du catalyseur $(ClO_4)_2Mg$ $[C_0] = 1{,}6 \times 10^{-3}$ mole/1: (+) calculé; (●) expérimentale.

l'agent catalytique, soit en rapport avec la concentration du monomère (Fig. 3).

Comme il résulte des diagrammes présentés sur la Figure 3, le diagramme calculé correspond avec le diagramme obtenu par l'expérience, surtout lorsqu'il s'agit de concentrations plus élevées de monomère.

D. Influence de la Temperature sur la Vitesse de Reaction

L'étude de l'influence de la température sur la vitesse de réaction s'est effectuée dans l'intervalle de température 20–40°C, et les résultats obtenus sont présentés sur le diagramme de la Figure 4.

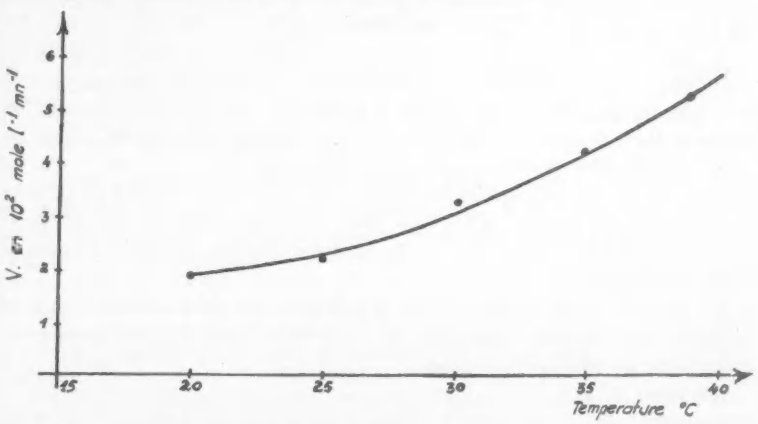

Fig. 4. Etude de la vitesse de polymérisation du *N*-vinylcarbazole par $(ClO_4)_2Mg$ à différentes températures; $[C_0] = 1{,}6 \times 10^{-3}$ mole/1 et $[M_0] = 1{,}25$ mole/1.

Comme il ressort de ce diagramme, la vitesse est influencée par l'élévation de la température et donne une bonne correspondance avec la relation d'Arrhenius.

En analysant les données cinétiques de la polymérisation du *N*-vinylcarbazole avec le perchlorate de magnésium anhydre, on constate que la vitesse de polymérisation V_p peut être représentée de façon satisfaisante par la relation

$$V_p = -dM/dt = K\,[c][M]$$

laquelle, après résolution conduit à l'expression:

$$\ln (M/M_0) = KC\tau$$

Comme il ressort des Figures 2 et 3, les résultats expérimentaux vérifient cette relation cinétique.

IV. DISCUTION

D'après les données expérimentales obtenues par nous les perchlorates peuvent être des catalyseurs efficaces dans la polymérisation des monomères vinyliques à grande densité d'electrons π sur la double liaison, si l'on assure la liberté cinétique du cation.

Les perchlorates sont des catalyseurs efficaces de la polymérisation cationique en phase homogène car ainsi se forme facilement la liaison metal–carbone qui dans ce cas est le véritable initiateur du processus de polymérisation.

On sait que le mécanisme de polymérisation cationique est basé, en général, sur l'attaque du proton sur la double liaison, le proton pouvant être libéré soit par le complexe (acide de Lewis et cocatalyseur) soit par les acides protoniques, soit par les pseudo-acides.[6]

Au cas où l'on utilise des persels du type perchlorates à cation mono ou bivallent, on peut réaliser la polymérisation cationique des monomères vinyliques avec une grande densité d'électrons π sur la double liaison, en réalisant les liaisons carbone–métal sur le compte du transfert de charge du cation perchlorate sur le méthylène du monomère.

Dans le cas des polymérisations effectuées dans des solvants polaires et à constante diélectrique faible $\epsilon = 6$–10, la dissociation des perchlorates s'est montrée suffisante pour que la liberté cinétique des cations perchlorates soit assurée.

En résumé, pour les persels qui contiennent un cation monovalent ou bivalent, les résultats présentés peuvent être discutés sur la base du mécanisme de réaction suivante.

Initiation:

$$(ClO_4)_2Me + CH_2{=}\underset{\displaystyle R}{\underset{|}{CH}} \rightarrow ClO_4MeCH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{\oplus}{\ominus}ClO_4$$

Propagation

$$ClO_4MeCH_2{-}\underset{R}{CH}{\oplus\ominus}ClO_4 + nCH_2{=}\underset{R}{CH} \rightarrow ClO_4Me(CH_2{-}\underset{R}{CH})_{n+1}{\oplus\ominus}ClO_4$$

Transfert avec le monomère:

$$ClO_4Me(CH_2{-}\underset{R}{CH})_{n-1}{-}CH_2{-}\underset{R}{CH}{\oplus\ominus}ClO_4 + CH_2{=}\underset{R}{CH} \rightarrow$$

$$ClO_4Me(CH_2{-}\underset{R}{CH})_{n-1}{-}\underset{R}{CH}{=}\underset{R}{CH} + CH_3{-}\underset{R}{CH}{\oplus\ominus}ClO_4$$

Transfert spontané de proton:

$$ClO_4Me(CH_2{-}\underset{R}{CH})_{n-1}{-}CH_2{-}\underset{R}{CH}{\oplus\ominus}ClO_4 \rightarrow ClO_4Me(CH_2{-}\underset{R}{CH})_{n-1}{-}\underset{R}{CH}{=}\underset{R}{CH} + HClO_4$$

Il est possible que dans ce cas aussi, de même que dans les cas de polymérisation du styrène avec l'acide perchlorique, décrits par Pepper[7,8] il n'existe pas de réaction de terminaison de chaînes, à proprement parler, à cause du processus de transfert spontané de proton.

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Résumé

La polymérisation des monomères vinyliques en milieu non aqueux peut être influencée par un grand nombre de sels minéraux. Dans ce cas les deux composants du sel, le cation et l'anion peuvent avoir un rôle actif. En poursuivant nos recherches sur la cinétique de la polymérisation avec des sels minéraux nous avons étudié le comportement des monomères vinyliques en présence de persels en milieu non aqueux. La cinétique de la polymérisation de monomères vinyliques en milieu non aqueux en présence de persels minéraux a été étudiée en fonction de la concentration en catalyseur, en monomère et en fonction de la température. Dans les solvants polaires l'ordre de la réaction par rapport à la concentration en catalyseur est égal à l'unité, quelque soit la concentration en monomère (par exemple *N*-vinylcarbazole); en outre il n'y a aucune polymérisation thermique. Dans ce cas de polymérisation, les solvants polaires avec une grande constante diélectrique sont les plus avantageux. Nous avons mis en évidence la possibilité de la polymérisation à grande vitesse à des températures basses non pas seulement par l'action du proton mais aussi par le cation. Après avoir établi la corrélation des résultats obtenus avec les théories connues, nous avons tâché de donner une interprétation du mécanisme du processus de polymérisation avec des persels en milieu non aqueux.

Synopsis

The polymerization of vinyl monomers in non-aqueous medium can be influenced by several inorganic salts. In this case, both components of the salt (cation and anion) can play an active role. In our further studies of the kinetics of polymerization with inorganic salts, we have studied the behavior of vinyl monomers in the presence of per-salts in non-aqueous medium. The kinetics of polymerization of vinyl monomers in non-aqueous medium in the presence of inorganic per-salts has been studied in function of the concentration of catalyst and of monomer and in function of the temperature. In polar solvents the order of reaction with respect to the catalyst concentration is equal to one, undependently of the monomer concentration (e.g., *N*-vinylcarbazol); moreover any thermal polymerization is absent. In these polymerization, the polar solvents with high dielectric constant are most advantageous. The possibility of polymerization with high velocities at low temperatures has been taken in evidence not only by the reaction of the proton, but as well by the cation. These results were correlated with previously existing theories; an interpretation of reaction mechanism of the polymerization with per-salts in non-aqueous medium has been given.

Zusammenfassung

Die Polymerisation von Vinylmonomeren in nichtwässrigem Milieu kann durch eine grosse Zahl anorganischer Salze beeinflusst werden. Es kann sowohl das Kation als auch das Anion in dieser Richtung aktiv sein. Im Verfolg unserer Arbeiten über die Kinetik der Polymerisation in Gegenwart von Mineralsalzen haben wir das Verhalten von Vinylmonomeren in Gegenwart von Persalzen in nichtwässrigem Milieu untersucht. Es wurde der Einfluss der Katalysator- und Monomerkonzentration sowie der Temperatur untersucht. In polaren Lösungsmitteln ist die Ordnung der Reaktion in bezug auf den Katalysator bei beliebiger Monomerkonzentration (z.B. *N*-Vinylcarbazol) gleich eins; thermische Polymerisation findet nicht statt. Bei dieser Polymerisation sind die polaren Lösungsmittel mit hoher Dielektrizitätskonstante am vorteilhaftesten. Es wurde gezeigt, dass eine Polymerisation mit grosser Geschwindigkeit bei tiefen Temperaturen nicht nur durch die Wirkung des Protons sondern auch durch die des Kations möglich ist. Die bekannten Theoren wurden auf die Versuchsergebnisse angewendet und ein Mechanismus für die Polymerisation mit Persalzen in nichtwässrigem Milieu angegeben.

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Cyclopolymerization of Isoprene in the Presence of $AlC_2H_5Cl_2$

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INTRODUCTION

The preparation of cyclopolymers from butadiene, isoprene, and chloroprene in the presence of Ziegler-type catalyst has been described in previous works[1,2] and infrared spectra of cyclopolymers were compared with those of cyclized 1,4 and 3,4 polyisoprenes.[3]

In this communication the preparation of cyclopolymers of isoprene in solution with $AlC_2H_5Cl_2$ as a catalyst is described, and the results of kinetic studies are presented. A mechanism of cyclopolymerization is proposed.

EXPERIMENTAL

The isoprene was free of water and dissolved gases and contained 2.2% pentene and 1.2% piperylene.

Catalyst

Ethylaluminum dichloride was synthesized by boiling a mixture of ethylsesquialuminum chloride with aluminum trichloride and isolated by distillation *in vacuo*. The purity was checked by means of infrared spectroscopy. No absorption bands characteristic of ethoxy groups were found in the infrared spectra.[4]

Solvents

Benzene, p.a. grade, and *n*-heptane, p.a. grade, were dried by refluxing over sodium dispersion and distilled *in vacuo* into glass ampules which were then sealed off.

Polymerization Reactions

All manipulations with monomer, solvents and catalyst solutions were carried out under vacuum in an apparatus which allowed a constant monomer concentration to be maintained in the solution.[5] The solvents and catalyst solution were delivered into the reaction vessel by breaking the glass ampules containing the respective liquids. The reaction vessel was

attached to a storage vessel containing a known amount monomer in a gaseous state. First, 40 ml. of a solvent was transferred into the reaction vessel, then the necessary amount of monomer was passed from the reservoir to give a solution of required concentration. The reaction was started by adding 2.5 ml. of the catalyst solution. A constant vapor pressure of monomer was maintained by admitting gaseous monomer from the storage vessel. The contents of the reaction vessel were vigorously stirred with a magnetic stirrer. The reaction products were precipitated in a nitrogen atmosphere with methanol, filtered, and centrifuged.

Polymerization reactions in *n*-heptane were carried out at temperatures ranging from −18° to 20°C. and in benzene at 20°C.

One attempt was made to carry out the polymerization of isoprene in the presence of $AlC_2H_5Cl_2 \cdot O(C_2H_5)_2$.

Infrared spectra were taken on a UR 10 (Jena) spectrophotometer in the range of 400–5000 cm.$^{-1}$ The measurements were made in CS_2 solution, on film deposited on a KBr plate, or by the KBr pellet technique.

The infrared spectra of the cyclopolymers treated *in vacuo* at 225°, 350°, and 525°C. for 1 hr. and in the air at 100°C. for 20 hr. were also studied.

RESULTS

The rate of disappearance of isoprene in *n*-heptane at various temperatures at a constant monomer concentration of 1.27 mole/l. and a constant catalyst concentration of 0.025 mole/l. is shown in Figure 1. Typical ki-

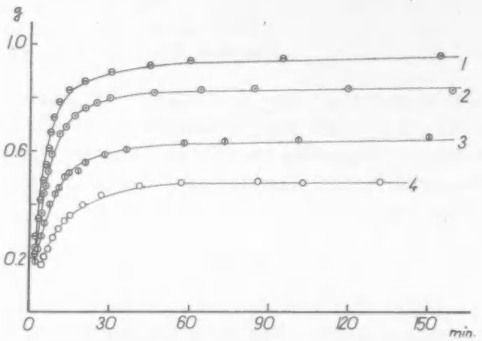


Fig. 1. Consumption of isoprene as a function of time at various temperatures: (1) 20°C.; (2) 13°C.; (3) 0°C.; (4) −18°C. Constant monomer concentration 1.27 mole/l., 40 ml. *m*-heptane, $AlEtCl_2$ concentration 0.025 mole/l.

netic curves representing the consumption of isoprene in benzene at 20°C. with 0.025 mole/l. of catalyst at four monomer concentrations are presented in Figure 2. The initial rate of polymerization was a linear function of the $AlC_2H_5Cl_2$ concentration.

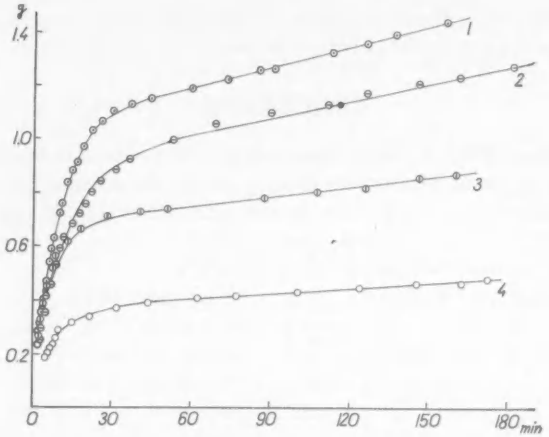


Fig. 2. Consumption of isoprene at various monomer concentrations at 20°C.: (*1*) 1.80 mole/l.; (*2*) 1.03 mole/l.; (*3*) 0.74 mole/l.; (*4*) 0.32 mole/l. In 40 ml. benzene. $AlEtCl_2$ concentration 0.025 mole/l.

In all experiments a white, powdery polymer was formed; it was of relatively low molecular weight, as characterized by low value of reduced viscosity $\eta_{red} = \eta_{sp}/c = 0.1$ at a concentration of 0.5 g./100 ml.

$AlC_2H_5Cl_2{\cdot}O(C_2H_5)_2$ was ineffective as a polymerization catalyst. The polymerization of isoprene in the presence of $AlC_2H_5Cl_2$ catalyst at a ratio of isoprene to $AlC_2H_5Cl_2$ of 100:1 in bulk proceeded very rapidly (in few seconds) to form an orange-colored polymer. When additional monomer was added after 20 hr., the polymerization started again very rapidly. The resulting polymer was a very hard, insoluble material; its infrared spectrum was very similar to that of cyclopolymers prepared in the presence of Ziegler-type catalyst.

The infrared spectrum of cyclopolyisoprene prepared in benzene at 20°C. with 0.025 mole/l. of $AlC_2H_5Cl_2$ and at a monomer concentration of 1.03

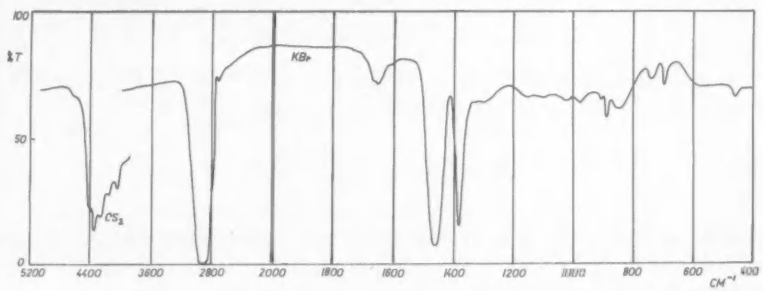


Fig. 3. Infrared spectrum of cyclopolyisoprene in KBr pellet (400–4000 cm.$^{-1}$) and in CS_2 solution (1.5%, 20 mm, 4000–5000 cm.$^{-1}$).

mole/l. after 3 hr. is shown in Figure 3. The absorption band at 700 cm.$^{-1}$ is absent in the spectra of polymers prepared in *n*-heptane.

DISCUSSION

Measurements of the rate of disappearance of isoprene in benzene shows the setting up of an equilibrium state in which the polymerization rate is about 30 times slower than it was in the initial state (Fig. 2). In heptane the decrease in the rate is much greater (Fig. 1). It follows that the catalyst looses its effectiveness, but not completely.

Ethylaluminium dichloride forms dimers, dissociating to ions of the type $Al(C_2H_5)_2^+ \cdot AlCl_4^-$, as proved by the relatively high electric conductivity,[6] NMR measurements,[7] and infrared spectroscopy.[4] $AlC_2H_5Cl_2$ is a strong electron acceptor, capable of complexing with halides of alkalic metals[8] and numerous electron donors, such as ethers and amines.

The ion pair $AlR_2^+ \cdot AlCl_4^-$ (A^+B^-) reacts with isoprene monomer to yield yellow complex $AlR_2^+ \cdot AlCl_4^- .M$ (CM). It is known that by coordination unsaturated salts of Al, B, Ti, etc., form π complexes with olefins. It may be supposed that dienes also form π complexes. The formation of π complexes is considered to be an initiation step.

The mechanism of the polymerization we propose is as follows:

$$A^+B^- + M \xrightarrow{k_i} (CM_1)$$

$$(CM_1) + nM \xrightarrow{k_p} (CM_{n+1})$$

$$(CM_m) \xrightarrow{k_t} M_m + A^+B^-$$

$$(CM_m) + M \xrightarrow{k_{trM}} M_m + (CM_1)$$

$$(CM_m) + (CM_n) \underset{k_2}{\overset{k_1}{\rightleftarrows}} (CM_m \cdot CM_n)$$

The active center (CM) forms dimers (CM·CM) of the type $AlR_2^+ \cdot AlCl_4^- \cdot M_m \cdot AlR_2^+ \cdot AlCl_4^- \cdot M_n$ incapable of polymerizing further monomers.

An equilibrium exists between the active centers (CM) and the inactive dimers (CM·CM). with the equilibrium constant

$$K = k_1/k_2 = \frac{[CM \cdot CM]}{[CM]^2} \tag{1}$$

Similar inactive dimeric polymer centers have been proposed by Cubbon and Margerison for the case of polymerization of styrene by *n*-butyllithium.[9]

The rate of disappearance of the monomer, A^+B^-, and CM are given by eqs. (2), (3), and (4), respectively.

$$-d[\mathrm{M}]/dt = \{k_i[\mathrm{A^+B^-}] + (k_p + k_{trM})[\mathrm{CM}]\}[\mathrm{M}] \quad (2)$$

$$-d[(\mathrm{A^+B^-})]/dt = k_i[\mathrm{A^+B^-}][\mathrm{M}] - k_t[\mathrm{CM}] \quad (3)$$

$$-d[\mathrm{CM}]/dt = -k_i[\mathrm{A^+B^-}][\mathrm{M}] + k_t[\mathrm{CM}] + k_1[\mathrm{CM}]^2 - k_2[\mathrm{CM{\cdot}CM}] \quad (4)$$

If c_0 represents the total concentration of $AlC_2H_5Cl_2$ which is present in the dimeric form, then

$$1/2C_0 = [\mathrm{A^+B^-}] + [\mathrm{CM}] + 2[\mathrm{CM{\cdot}CM}] \quad (5)$$

From the plot of the rate of isoprene disappearance against time in the initial stage of the reaction it can be seen that the consumption of monomer corresponds to the formation of a complex of A^+B^- just with one monomer molecule. This reaction is very fast and proceeds practically immediately. The formation of the complex (CM) is accompanied by coloration of the mixture. The intensity of the color is unchanged during the entire reaction.

In the stationary state

$$d[(\mathrm{CM})]/dt = 0$$

and

$$\frac{d[\mathrm{A^+B^-}]}{dt} = 0 \quad (6)$$

and then

$$-\frac{d[\mathrm{M}]}{dt} = \{k_t + (k_p + k_{trM})[\mathrm{M}]\}[\mathrm{CM}]$$

By assuming that $k_p[\mathrm{M}] > k_{trM}[\mathrm{M}]$ and after neglecting the term $k_t[\mathrm{CM}]$ in comparison with the term $(k_p + k_{trM})][\mathrm{CM}][\mathrm{M}]$ we obtain

$$-d[\mathrm{M}]/dt = k_p[\mathrm{CM}][\mathrm{M}] \quad (8)$$

In the initial stage ($t \rightarrow 0$), the concentration of the inactive dimer (CM·CM) is supposed to be equal to zero and also the concentration of the uncomplexed catalyst A^+B^- is equal to zero after a very short period of the reaction.

Substituting from eq. (5) yields

$$-(d[\mathrm{M}]/dt)_{t\rightarrow 0} = 1/2k_pc_0[\mathrm{M}] \quad (9)$$

The rate of isoprene disappearance at $t \rightarrow 0$ was determined from the initial slopes of monomer–time curves. The dependence of the initial rate on monomer concentration is shown in Figure 4. The reaction is linear with [M] as follows from eq. (7). The dependence of the initial rate on catalyst concentration was found to be linear, which corresponds to eq. (7).

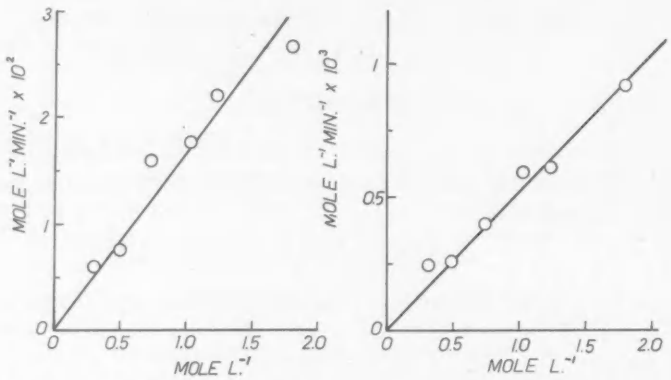


Fig. 4. Plot of initial rate of polymerization as a function of monomer concentration.
Fig. 5. Rate of polymerization in the equilibrium state as a function of monomer concentration.

The rate constant k_p at 20°C., as determined from eq. (7) is 1.28 l./mole-min., and the activation energy was found to be 3.7 kcal./mole.

After 30–50 min. an equlibrium was set up between the active centers (CM) and inactive dimers (CM·CM). Also in this case $[A^+B^-] = 0$, and using eq. (5) and substituting into eq. (1) we obtain

$$2[CM]^2K + [CM] - 1/2c_0 = 0 \tag{10}$$

and

$$-(d[M]/dt)_{t\to\infty} = k_p[M][-1 + (1 + 4Kc_0)^{1/2}]/4K \tag{11}$$

The rate of polymerization at $t \to \infty$ is in linear dependence on monomer concentration (see Fig. 5). Using the value for k_p we calculate

$$K = 3.8 \times 10^4 \text{ l./mole}$$

In *n*-heptane the value of K is higher than in benzene, and thus the rate of polymerization at $t \to \infty$ is very slow (Compare Figs. 1 and 2).

The value of $k_pK^{1/2}$ is 1.12×10^{-4} l.$^{1/2}$/mole$^{1/2}$ sec. This is about one fiftieth of the value found in the polymerization of styrene initiated by butyllithium.[9]

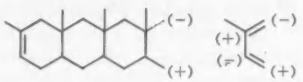
In the interpretation of infrared spectra it has been observed that cyclopolymers prepared in benzene contain small amount of phenyl groups. The initial rates of polymerization in *n*-heptane and in benzene were, however, practically the same under the same conditions.

When the polymerization was carried out in bulk the formation of inactive dimers (CM·CM) was retarded because of the lowered mobility of the active centers in the highly viscous medium.

In all experiments cyclopolymer was formed, which is evident from the comparison of infrared spectra and properties with those of cyclopolymers

obtained in the presence of Ziegler-type catalyst.[1,2] Infrared spectra of polymer film deposited on KBr plate differ from spectra of the KBr pellet by a shift of the bands at 1150 and 1100 cm.$^{-1}$ of about 20 cm.$^{-1}$ toward lower wave numbers.

On the basis of the proposed structure[2] it may be supposed that the polymerization proceeds according to the scheme



which does not involve the separation of AlR_2^+ and $AlCl_4^-$ ions. In the chain transfer through the monomer the effective catalyst is recovered. The support of the proposed recovery of $AlR_2^+ \cdot AlCl_4^-$ catalyst is that stereoregular polymer is produced containing less than 3% of 1,4 or 3,4 addition. If in the chain transfer reaction catalyst of the type $AlCl_3 \cdot HCl$ is formed, the polymer should contain more "usual" structures.

$AlC_2H_5Cl_2 \cdot O(C_2H_5)_2$ is ineffective as a polymerization catalyst because of the strong complexing capacity of ether.

According to the proposed scheme, the polymer chain contains three types of double bonds: vinyl or isopropenyl in one chain end and internal C=C in the ring in the opposite end. In the infrared spectrum we can find very weak absorption bands at 910 and 890 cm.$^{-1}$ which are characteristic of vinyl and vinylidene groups, respectively.

These bands may be due to only terminal unsaturation; if this is so, it would mean that the purity of the cyclic structure is even higher than the value found (97%).

Two very weak bands at 1645 and 1665 cm.$^{-1}$ are present in the spectrum. The first is due to vinyl or vinylidene type C=C; the second probably indicates the presence of terminal unsaturation in the ring.

On heating in the air at 380°C. the polymer changes from a solid to a liquid. The infrared spectrum of the sample heated to 350°C. *in vacuo* indicates only minor changes in the range of C=C vibrations. A new weak band is observed at 1620 cm.$^{-1}$ After 1 hr. *in vacuo* at 525°C. the polymer partially decomposes, and methane and hydrogen are isolated. Even at this temperature no change in the infrared spectrum is observed, except a slight increase in the intensity of the 1620 cm.$^{-1}$ band.

The rate of oxidation of the cyclopolyisoprene in air at 100°C. is much lower than that of oxidation of linear 1,4-polyisoprene.

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Synopsis

Polymerization of isoprene in the presence of $AlC_2H_5Cl_2$ in benzene, *n*-heptane, and in bulk leads to the formation of white, powdery polymers having cyclic structures. Kinetics of the polymerization has been studied at the constant monomer concentration. The relatively high rate of polymerization in the initial stage decreases to some limiting value, dependent on the solvent used. The rate of polymerization is linearly dependent on monomer concentration. The initial rate is proportional to the catalyst concentration. Assuming that the rate of initiation is very high the rate constant of propagation has been calculated at 20°C. in benzene to be $k_p = 1.28$ l./mole-min. The activation energy was calculated as $E = 3.7$ kcal./mole. The active centers at the polymer chain ends form dimer incapable of participating in the propagation, which is in an equilibrium with the active centers. The equilibrium constant of this interaction is $K = 3.8 \times 10^4$ l./mole.

Résumé

La polymérisation de l'isoprène en présence d'$AlC_2H_5Cl_2$ dans le benzène, l'heptane-*n* et en bloc conduit à la formation de polymères poudreux blancs à structure cyclique. On a étudié la cinétique de polymérisation à concentration constante en monomère. La vitesse relativement élevée de polymérisation dans l'étape initiale diminue vers une valeur limite, dépendant du solvant utilisé. La vitesse de polymérisation est une fonction linéaire de la concentration en monomère. La vitesse initiale est proportionnelle à la concentration du catalyseur. Dans l'hypothèse d'une vitesse d'initiation très élevée, on a calculé la constante de vitesse de propagation à 20°C dans le benzène $k_p = 1.28$ l mole^{-1}min^{-1}. On a calculé l'énergie d'activation $E = 3.7$ kcal mole^{-1}. Les centres actifs en fin de chaîne polymèrique forment des dimères incapable de participer à la propagation, qui sont en èquilibre avec les centres actifs. La constante d'équilibre de cette interaction est $K = 3.8 \times 10^4$ l mole^{-1}.

Zusammenfassung

Die Polymerisation von Isopren in Gegenwart von $AlC_2H_5Cl_2$ in Benzol, *n*-Heptan und in Substanz führt zur Bildung weisser, pulvriger Polymerer mit cyclischer Struktur. Die Polymerisationskinetik wurde bei konstanter Monomerkonzentration untersucht. Die relativ hohe Anfangsgeschwindigkeit der Polymerisation fiel auf einen vom verwendeten Lösungsmittel abhängigen Grenzwert ab. Die Polymerisationsgeschwindigkeit zeigt eine lineare Abhängigkeit von der Monomerkonzentration. Die Anfangsgeschwindigkeit ist der Katalysatorkonzentration proportional. Unter der Annahme einer sehr hohen Startgeschwindigkeit wurde die Wachstumsgeschwindigkeitskonstante bei 20°C in Benzol zu $k_p = 1{,}28$ l Mol^{-1} min^{-1} berechnet. Die Aktivierungsenergie ergab sich zu $E = 3{,}7$ kcal/Mol. Die aktiven Zentren am Ende der Polymerkette bilden ein zur Teilnahme am Wachstum unfähiges Dimeres, das mit den aktiven Zentren im Gleichgewicht steht. Die Gleichgewichtskonstante dafür beträgt $K = 3{,}8 \times 10^4$ l Mol^{-1}.

Discussion

B. Eroussalimsky (*Leningrad, U.R.S.S.*): If this is a cationic system must one believe that here a catalyst is not necessary?

I. Kössler: We used very carefully dried materials and no cocatalyst was added.

B. Eroussalimsky: Have you some data about the influence of water on the polymerization rate?

I. Kössler: We suppose that water is not involved in the formation of a catalytic complex. In the presence of small amounts of water the polymerization should be "free cationic" as in the case of $AlCl_3 \cdot H_2O$ and should yield a polymer with more 1,4 structures. It may be mentioned that in the presence of ether (Al:ether = 1:1) the catalyst is inactive.

B. Seidel (*Cologne, Germany*): Have you observed the cyclopolymers that you described in your system exclusively or have you also obtained cyclopolymers of the type reported by Wilke (Spring Meeting of the American Chemical Society, Boston, 1959, and later references) i.e., cyclodedecatriene?

I. Kössler: According to I. R. analysis, the polymer prepared with $AlEtCl_2$ contains less than 5% of usual structures 1,4 or 3,4. With Ziegler–Natta catalyst (ref. 1,2) we obtained polymers which are stereoblocks of linear and cyclic structures.

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Nitrogen-Containing Radical-Ions as Initiators for Vinyl Polymerizaton

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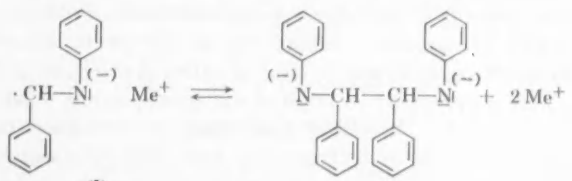
I. INTRODUCTION

The reaction of Schiff bases with alkali metals yields deeply colored, very reactive, N-containing radical-ions.[1] In analogy to the carefully investigated metal ketyls,[2,3] these radical-ion pairs (I) are in an equilibrium with dianions (II), as described for the benzylidene aniline derivative:



(I) (II)

where Me is an alkali metal. The unpaired electron and the negative charge of the radicalanion are not completely localized. Only the possibility that the unpaired electron is on the nitrogen and the anion on the carbon can be ruled out on energy grounds.[4]

Investigations on the activity of metal ketyls as polymerization catalysts were described recently.[5–8] The monoalkali metal complexes of aromatic ketones, e.g., benzophenone, were found to induce the polymerization of easily anionically polymerizing monomers. Styrene was only polymerized by the dimetal complexes to give a "living" system. Based on copolymerization studies it was proposed that the polymerization was initiated by the alkoxide part of the ketyl molecule.

This paper describes the initiation of vinyl monomers with N-containing radical-anions prepared by reaction of several Schiff bases with potassium, sodium, and lithium. In contrast to the metal ketyls which can only be prepared from nonenolizable ketones, the preparation of the metal–Schiff base complexes is possible from aliphatic and aromatic amines, ketons and aldehydes. The following Schiff bases were used: benzylidene aniline, 4-diethylaminobenzylidene aniline, benzylidene 4-methoxyaniline, benzylidene isopropylamine, pyridine 4-aldehyde anil, and cinamylidene aniline.

II. EXPERIMENTAL

Materials

In order to avoid any inhibition by carbon dioxide, water, or oxygen all preparations were carried out under purified nitrogen. Nitrogen was freed from oxygen by passage through a set of 1:3 solution of dipotassium benzophenone in xylene–dioxane (1:1) mixtures.

Solvents. Benzene, toluene, hexane, and tetrahydrofuran were refluxed with potassium and benzophenone until the blue color of the complex persisted throughout the mixture. Immediately before use all solvents were redistilled under nitrogen and in the presence of dipotassium benzophenone.

Monomers. Styrene, methyl methacrylate, and acrylonitrile were purified by successive washings with dilute sodium hydroxide solutions (3%) and water, dried over sodium sulfate, and twice distilled under prepurified nitrogen. Middle fractions were used for the polymerization experiments: styrene, b.p. 36°C./12 mm.; methyl methacrylate, b.p. 40°C./74 mm.; acrylonitrile, b.p. 77°C.

Schiff Bases. Benzylidene aniline,[9] m.p. 54–55°C., benzylidene isopropylamine, b.p. 39°C./0.1 mm., 4-diethylaminobenzylidene aniline,[10] m.p. 108–109°C., cinamylidene aniline,[11] m.p. 108–109°C., benzylidene 4-methoxyaniline,[12] m.p. 63–64°C., and pyridine 4-aldehyde anil,[13] m.p. 72–73°C., were prepared by reaction of the corresponding aldehydes and amines in methanol. The Schiff bases were recrystallized once from methanol and once from cyclohexane and dried over P_2O_5 and paraffin at 65°C./0.1 mm. for 3 days. Benzylidene isopropylamine was twice redistilled under nitrogen.

Poly(benzylidene 4-vinylaniline)[14] and poly(cinamylidene 4-vinylaniline[14] were prepared by radical-induced polymerization of the corresponding monomers[14] in a 20% benzene solution; benzoyl peroxide and azobisisobutyronitrile were used as initiators (2 wt.-%). The low molecular weight polymers were purified by dissolution in benzene and precipitation from methanol and ether. Constants for poly(benzylidene 4-vinylaniline) were $[\eta] = 0.036$, softening point range = 100–110°C.; for poly(cinamylidene 4-vinylaniline); $[\eta] = 0.055$, decomposition temperature 250–280°C.

Preparation of the Catalyst Solutions

The catalysts were prepared in Schlenk tubes which were flamed under purified nitrogen before use. Schiff base (4–5 g.) was dissolved in 50 ml. of absolute tetrahydrofuran, an equivalent amount of an alkali metal was added, and the mixture was shaken at room temperature until there was no metal left (1–10 hr.). The intense color of the ion-radical (yellow, red, or brown, depending on the structure of the Schiff bases and the alkali metals) appeared in a few seconds. The yields (96–98%) were determined by titration of the filtered solutions.

The dimetal complexes were prepared by the same method using an excess of the metal.

Polymerization

The polymerizations were carried out under nitrogen in carefully flamed Schlenk tubes. The monomer (5 ml.) and the solvent (10 ml.) were cooled to the required temperature (usually 0°C.), and the catalyst (1–3 mole-%) was added with a syringe through a self-sealing rubber stopper. The polymerization was terminated after the required time by addition of methanol. The polymers were precipitated from methanol. Poly(methyl methacrylate) was purified by dissolution in benzene and reprecipitation from methanol, polyacrylonitrile by dissolution in dimethylfumamide and reprecipitation from methanol. The analysis of the copolymers were performed by A. Bernhardt, Microanalytical Laboratories, Mülheim/Rhur, Germany.

Viscosities

The viscosities of the poly(methyl methacrylates) were determined in benzene solution at 28 ± 0.05°C. Solution and solvent were filtered through a sintered glass disk before each determination. The Ostwald viscometer had a flow time of 113.0 sec. for pure benzene. The average molecular weights were calculated from the intrinsic viscosities by use of eq. (1):[15]

$$\log \bar{M}_v = (\log [\eta] + 4.284)/0.76 \quad (1)$$

Graft Polymerization

The technique described above was also used for the polymerization of methyl methacrylate and acrylonitrile with the macromolecular polyfunctional initiators. The graft polymers prepared with acrylonitrile were soluble in dimethylformamide but completely insoluble in chloroform. Extraction with chloroform in a Soxhlet apparatus for 3 days did not yield any soluble products. The infrared spectra of the polymers before and after the extraction were identical. The graft polymers prepared with methyl methacrylate were completely soluble in chloroform, benzene, and tetrahydrofuran.

III. RESULTS

1. Catalytic Activity of Mono- and Dimetal Complexes of Schiff Bases

The activity of N-containing radical-anions and of the corresponding dimetal complexes as initiation catalysts for the vinyl polymerization may be demonstrated by the metal complexes of benzylidene 4-methoxyaniline. The results are given in Table I.

Acrylonitrile and methyl methacrylate are rapidly polymerized by the N-containing radical-anion. Although far more reactive than potassium ketyls,[6,7] it still does not initiate the polymerization of styrene. The carbanion-containing dimetal complex has a greater activity and—as expected—is a very good initiator for styrene, too. The red color of the

TABLE I
Polymerization of Acrylonitrile, Methyl methacrylate, and Styrene by the Benzylidene 4-Methoxyaniline Metal Complexes at 0°C.

Initiator[a]		Monomer	Solvent		Conversion,
Metal	Mole-%	(5 ml.)	(10 ml.)	Time	%[b]
Monopotassium complex	1.0	Acrylonitrile	Benzene	0.5 min.	10.5
"	1.0	"	"	2.0 min.	9.8
"	1.6	Methyl methacrylate	"	2.0 min.	83.2
"	1.5	Styrene	"	2.0 min.	—
"	1.5	"	"	15 hr.	—
Dipotassium complex	0.5	Acrylonitrile	Hexane	—	Explosive
"	0.5	Methyl methacrylate	"	20 sec.	90.0
"	0.5	Styrene	Benzene	17 sec.	75.3

[a] The catalysts were dissolved in tetrahydrofuran (8–12 wt.-%).

[b] The yields on polyacrylonitrile depend strongly on the polymerization conditions. Extensive stirring was necessary. High yields were obtained only when the monomer was added to the initiator solution. Thus the yields on polyacrylonitrile and poly(methyl methacrylate) cannot be compared.

benzyl anion was observed in styrene bulk polymerization. When freshly distilled styrene was added to a polymerization run after a few hours at −50°C. the polymerization started again and an increase in the molecular weight of the polystyrene was observed. Thus it is probable to assume the formation of "living polymers" with the dimetal complexes as shown for the corresponding benzophenone derivative.[7]

2. Copolymerization

The composition of styrene and methyl methacrylate or acrylonitrile copolymers may be used as a criterion of the type of propagation induced by a given initiator.[16] Knowing that other complicating factors can arise[17,18] the copolymerization of styrene, methyl methacrylate, and acrylonitrile was studied. All copolymerizations were carried out in benzene at 0°C. The copolymer compositions are given in Tables II and III.

The results given in Table II show that the copolymerization at least with the potassium and sodium containing catalysts is typically anionic. This is still underlined by the copolymerization data of acrylonitrile, methyl methacrylate, and styrene as given in Table III. The polymers isolated in the copolymerization of acrylonitrile with styrene were shown to be pure polyacrylonitrile.

In agreement with similar data given for the ketyl-initiated copolymerization,[8] the metal component of the initiator system seems to influence the copolymer composition. The higher the electropositivity of the metal, the

TABLE II
Copolymerization of Methyl Methacrylate with Styrene[a]

Initiator		Conversion, %	Methyl methacrylate in the copolymer, mole-%[b]
Schiff base	Metal		
Cinamylidene aniline	K	17.0	100.0
Benzylidene aniline	Na	12.9	98.2
Benzylidene 4-methoxyaniline	K	10.5	100.0
"	Na	5.1	98.1
4-Diethylamino-benzylidene aniline	K	9.2	100.0
"	Na	17.2	98.2
"	Li	7.3	97.1

[a] Initial concentration of methyl methacrylate: 51.7-mole-%; initiator concentration: 1.5–2.5 mole-%.

[b] The values are an average of two runs.

TABLE III
Copolymerization of Acrylonitrile (M_1) with Methyl Methacrylate (M_2) or Styrene (M_2)

Initiator		M_1 in initial mixture, mole-%	M_2	Conversion, %	M_1 in the copolymer, mole-%
Schiff base	Metal				
4-Diethylamino-benzylidene aniline	K	63.3	Styrene		100.0
"	Na	"	"	4.7	99.8
"	Li	"	"	5.2	99.8
Cinamylidene aniline	K	61.6	Methyl methacrylate	17.0	95.2
"	Na	"	"	7.8	92.1
"	Li	"	"	6.1	89.1

higher the degree of incorporation of methyl methacrylate (Table II) or acrylonitrile (Table III) into the copolymer.

3. Influence of the Structure of the Schiff Base

All initiators studied induced the polymerization of acrylonitrile and methyl methacrylate, even at −60°C. Their catalytic activity depends strongly on the structure of the Schiff base used for their preparation, as shown in Tables IV and V for different sodium and lithium complexes.

4. Influence of the Solvent and of the Metal

The influence of the solvents on the polymerization of methyl methacrylate by N-radical-anions was perceptible. For sodium and potassium-

TABLE IV

Polymerization of Methyl Methacrylate (5 ml.) by Various Monosodium Schiff Base Complexes in Benzene (10 ml.) at 0°C.

Initiator		Time, min.	Conversion, %	$\bar{M}_v \times 10^{-4}$	Catalyst color and change[a]
Schiff base	Mole-%				
Benzylidene aniline	2.0	1	84.0		Red; instantaneous
Benzylidene 4-methoxyaniline	1.8	2	65.8	4.7	Red; instantaneous
4-Diethylamino-benzylidene aniline	1.4	5	64.3	5.2	Dark orange; fast
Benzylidene isopropylamine	2.3	5	39.3	5.3	Red; fast
Cinamylidene aniline	1.8	5	31.2	2.1	Red-brown; no color change

[a] Color of the catalyst solution and speed of change of the color during the polymerization to a yellow amber.

TABLE V

Polymerization of Methyl Methacrylate (5 ml.) by Various Monolithium Schiff Base Complexes in Benzene (10 ml.) at 0°C.

Initiator		Time, min.	Conversion, %	$\bar{M}_v \times 10^{-4}$	Catalyst color and change[a]
Schiff base	Mole-%				
Benzylidene 4-methoxy-aniline	1.9	2	63.3	4.9	Red; fast
4-Diethylaminobenzy-lidene aniline	1.7	5	65.1	5.7	Yellow-brownish; fast
Cinamylidene aniline	2.0	5	48.1	2.1	Red; no change
Benzylidene isopropyl-aniline	2.6	12	23.3	6.8	Red; instantaneous

[a] Color of the catalyst solution and change of the color during the polymerization to a yellow amber.

TABLE VI

Polymerization of Methyl Methacrylate at 0°C. in Various Solvents

Initiator			Solvent	Time, min.	Conversion, %
Schiff base	Metal	Mole %			
Pyridine 4-aldehyde anil	K	2.4	Tetrahydro-furan	85	93.4
"	K	2.4	Benzene	85	55.0
Benzylidene aniline	Na	2.0	Benzene	1	84.0
"	Na	2.0	*n*-Hexane	1/6	89.4
Cinamylidine aniline	Na	1.8	Benzene	5	31.2
"	Na	1.8	*n*-Hexane	5	37.2
Benzylidene 4-meth-oxyaniline	Na	1.8	Tetrahydro-furan	2	82.5
"	Na	1.8	Hexane	5	62.2

containing initiator systems the highest yields were found in tetrahydrofuran. The polymerization rates in benzene and hexane did not differ very much, but were higher in hexane than in benzene. (Table VI).

The influence of the metal and the solvent on the catalytic activity of N-radical-anions depend on each other.

In tetrahydrofuran and benzene the activity of the complexes is proportional to the electropositivity of the metal, as shown in Tables VII and VIII. In *n*-hexane the lithium-containing complex has the highest catalytic activity, as shown in Tables VII and VIII.

TABLE VII

Polymerization of Methyl Methacrylate (5 ml.) with Benzylidene 4-Methoxyaniline Monometal Complexes at 0°C.

Solvent (10 ml.)	Metal	Initiator, mole-%	Time, min.	Conversion, %
Benzene	K	1.6	2	83.2
"	Na	1.8	2	65.8
"	Li	1.9	2	63.3
n-Hexane	Na	1.8	5	62.2
"	Li	1.9	5	92.2

TABLE VIII

Polymerization of Methyl Methacrylate (5 ml.) with Benzylidene Isopropylamine Monometal Complexes at 0°C.

Solvent (10 ml.)	Metal	Initiator, mole-%	Time, min.	Conversion, %
Tetrahydrofuran	K	2.2	5	76.0
"	Na	2.3	5	44.0
"	Li	1.3	5	19.7
"	Li	2.6	5	27.6
"	Li	3.9	5	33.2
n-Hexane	K	2.2	5	55.9
"	Na	2.3	5	12.2
"	Na	2.3	10	14.5
"	Li	2.6	5	79.1

5. Preparation of Graft Copolymers

In connection with investigations on vinyl Schiff bases[14] we have been interested to test the catalystic activity of macromolecular N-containing radical-anions. The initiation of vinyl monomers by polyvinylbenzophenone-sodium was recently described by Greber and Egle.[19] Qualitative experiments with the monopotassium complexes of polybenzylidene 4-vinylaniline and polycinamylidene 4-vinylaniline showed that these polymeric initiators can be used for anionic graft copolymerizations. The results are given in Table IX.

TABLE IX
Graft Copolymerization of Methyl Methacrylate (5 ml.) and Acrylonitrile (5 ml.) with Monopotassium Complexes of Macromolecular Polyfunctional Schiff Bases at 0°C. in Tetrahydrofuran

Polymeric Schiff Base	Initiator, mole-%	Monomer	Time	Conversion, %	Color of catalyst solution
Polybenzylidene-4-vinylaniline	0.32	Acrylonitrile	2 min.	14.3	Red-brown[a]
"	0.80	"	5 sec.	23.3	"
"	0.62	Methyl methacrylate	2 min.	8.1	"
"	1.60	"	2 min.	39.1	Orange-red[a]
Polycinamylidene-4-vinylaniline	0.20	Acrylonitrile	10 min.	17.0	"
"	0.45	Methyl methacrylate	28 min.	10.7	"

[a] Slow color change of the reaction mixture to a yellow amber.

The graft copolymers with acrylonitrile were soluble in dimethylformamide, but completely insoluble in chloroform, which is a good solvent for both polyvinyl Schiff bases. The infrared spectra of the graft copolymers before and after the extraction with chloroform were identical. The copolymers with methyl methacrylate are completely soluble in chloroform, benzene, and tetrahydrofuran.

The fact that the graft copolymers are completely soluble does not permit explanation of the disappearance of the free radicals formed during the initiation step by recombination. Reactions with impurities or hydrogen abstraction are possible. A detailed study on this topic will be subject of a subsequent paper.

IV. DISCUSSION

Theoretically the initiation of vinyl monomers by N-containing radical-anions may proceed at both the ionic or the radical end of the complex as discussed by O'Driscoll and Tobolsky[17] for the lithium-initiated polymerization.

$$\cdot\mathrm{CH}(\mathrm{R})\text{—}\mathrm{N}^{-}\mathrm{M}^{+} \xrightarrow{\text{monomer (M)}} \cdot\mathrm{M}\text{—}\sim\sim\text{—}\mathrm{CH}(\mathrm{R})\text{—}\mathrm{N}^{-}\sim\sim\mathrm{M}^{+}$$

These possibilities were studied by copolymerization of styrene, methyl methacrylate, and acrylonitrile as shown in Tables II and III. The results favor an anionic initiation step. Although the benzyl radical is very active and not as stabilized as the diphenylmethyl radical in the polymerization reaction with ketyls,[6] it does not seem to take part in the initiation step but is probably stabilized by recombination or hydrogen abstraction.

One could also consider an electron transfer-type initiation[20] which is ruled out by the fact that macromolecular polyfunctional N-containing radical-anions are active initiators for graft copolymers (Table IX). Thus one can assume that the polymerization is started by the nitrogen anion. Further studies will be necessary to elucidate the special activity of the used catalyst systems. N-containing radical-anions are quite different in reactivity from regular metal amides. Investigations in this direction connected with ESR measurements of the N-containing radical-anions are in process. These studies have already shown that a radical-induced polymerization of styrene with these initiator systems is possible if the anion is trapped by titration with an acid chloride or an active alkyl halide.

The high initiation activity of the dimetal complexes which is caused by the carbanion was not yet further investigated.

Especially the polymerization with lithium-containing complexes led to crystallizable polymethyl methacrylates. Their infrared absorption spectra are identical with the spectra of poly(methyl methacrylate) described by Furukawa et al. as F-type polymers.[21]

The influence of the structure of the Schiff base used for the preparation of the initiation complex is not only caused by the N-substituent, i.e., by the amine but also by the aldehyde component. If one compares the three benzaldehyde derivatives benzylidene aniline, benzylidene 4-methoxyaniline, and benzylidene isopropylamine, it can be shown that the basicity of the amine lowers the catalytic activity of the metal complex (Tables IV and V).

Besides the structure of the initiators, the nature of the counterion and the solvent are factors contributing to the rate and the direction of anionic initiation. The polymerization experiments described in Tables VII and VIII indicate a proportionality between the electropositivity of the counterion and the initiation activity of the complexes in tetrahydrofuran and benzene. This is in agreement with findings of Goode, Snyder, and Fettes, who studied the polymerization of vinyl monomers with various metal amides in liquid ammonia.[22]

The influence of the solvent on the polymerization rate as shown in Table VI can be explained in terms of the increasing ionic character of the propagating center. For the highly ionic potassium and sodium complexes the highest yields were found in tetrahydrofuran. But the polarity of the solvents may also influence the initiation step by changing the degree of dissociation of the dianion (II) to the radical-anion (I) or by changing the equilibrium between the radical-anion (III) and the ion pair (V)

$$\underset{\text{(III)}}{Me^{(+)}\,\overset{\cdot}{(-)}\,N{-}CH_2\cdot} \rightleftarrows \underset{\text{(V)}}{\overset{\cdot}{Me}{-}N{-}CH_2\cdot}$$

The effect of the solvent on the specific cation–anion interaction of alkali ketyls was shown by Garst et al.[23] This effect may overlap the influence of the solvent on the propagating center and seems to be especially important

for the lithium-containing initiator systems. It was found that the conditions leading to the most covalent type of a nitrogen-lithium bond, e.g., in *n*-hexane (Tables VII and VIII), gave the highest yields of poly(methyl methacrylate).

This research was supported by the Deutsche Forschungsgemeinschaft. The author is indebted to Prof. Dr. F. H. Müller for his support and his interest in this work. Grateful acknowledgment is also made to Mrs. U. Frederichs for her help in this work.

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Synopsis

The alkali metal complexes of Schiff bases were found to induce the polymerization of easily anionically polymerizing monomers, e.g., acrylonitrile and methyl methacrylate. The dimetal complexes which had a higher activity than the *N*-radical-anions polymerized styrene too. The metal complexes of macromolecular polyfunctional Schiff bases were used to prepare graft copolymers. Copolymerization studies showed the polymerization to be anionic. The structure of the Schiff bases as well as the nature of the metals and the solvents affected the activity of the radical-anions.

Résumé

Nous avons mis en évidence que les complexes des bases de Schiff de métaux alcalins induisent la polymérisation de monomères qui polymérisent facilement de manière anionique, entre autre l'acrylonitrile et le méthacrylate en présence de complexes dimétalliques qui ont une plus grande activité que les *N*-radicauxanions. Nous avons

utilisé les complexes métalliques des bases de Schiff macromoléculaires et polyfonctionnelles pour préparer des copolymères greffés. Par des études de copolymérisation, on a démontré que la polymérisation était anionique. L'activité des radicaux-anions est affectée aussi bien par la structure des bases de Schiff que par la nature des métaux et du solvant.

Zusammenfassung

Die Alkalimetallkomplexe von Schiff'schen Basen erwiesen sich als aktive Initiatoren leicht anionisch polymerisierbarer Vinylverbindungen, wie z.B. Acrylnitril und Methacryl säuremethylester. Mit den Dimetallkomplexen, die eine höhere Aktivität aufweisen als die stickstoffhaltigen Ionenradikale, konnte auch Styrol polymerisiert werden. Die Metallkomplexe makromolekularer, polyfunktioneller Schiff'scher Basen wurden als Initiatoren zur Darstellung von Pfropfpolamerisaten verwendet. Durch Copolymerisationsversuche konnte gezeigt werden, dass die Polymerisation typisch anionisch verläuft. Die Struktur der Schiff'schen Base, die Metallkomponente und das Lösungsimttel beeinflussen die Aktivität der verwendeten Initiatoren.

Discussion

K. Letarte (*France*): Could you please say anything more about the polymerization of your polyvinyl Schiff bases?

H. Ringsdorf: The vinyl Schiff bases were prepared by reaction of 4-vinylaniline (dehydration of HO—CH_2—CH_2— —NH_2) with benzaldehyde, pyridinaldehyde, and cinamylaldehyde. The monomers were polymerized with azoisobutyronitrile in benzene to yield soluble polymers. The bulkpolymerization yielded crosslinked compounds due to the —N=CH— group, which seems to take part in the polymerization.

M. Willner (*Italie*): I have two questions: the first concerning the graft copolymerization with your dimetall complexes: can they transfer electrons to yield homopolymers?

And the second question: did you ever use toluene as solvent and when yes how did this solvent influence the polymerization?

H. Ringsdorf: (1) Fractionation of graft copolymers prepared from polyvinyl Schiff base–dimetal complexes and methylmethacrylate yielded up to 15% of linear polymethylmethacrylate probably due to an electron transfer type initiation.

(2) Yes, we run several polymerizations in toluene. The results are similar to those found when we polymerized in tetrahydrofuran. The yields were lower, but also proportional to the electropositivity of the used metal.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 999–1007

Low Temperature Polymerization of Chlorosubstituted Aldehydes

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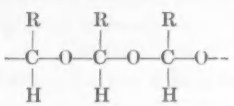
Low-temperature polymerization of aldehydes is one of the most promising methods for obtaining stereoregular polymers of the polyether type. In recent years results of theoretical interest have been obtained in this line. Among a group of monomers polymerizing effectively at low temperatures with various types of catalysts, which deserve attention apart from the extensively studied carbonyl compounds, are chlorine-substituted aldehydes, particularly, trichloroacetaldehyde or chloral, which is a commercial product.

It is known[1–6] that aldehydes polymerize readily with cationic and anionic catalysts. Chlorine-substituted aldehydes are still more reactive compounds in the polymerization reaction, because they contain chlorine atoms having a high inductive effect. Polymerization occurs readily at the carbonyl bond, yielding a polymer of the type:



where R may be an alkyl or various halogen-substituted alkyls. Preliminary tests showed that the best catalyst among the metalloorganic compounds for low temperature polymerization of chloral was butyllithium, and therefore all the subsequent experiments were performed with this catalyst.

Polymerization of chloral was carried out in *n*-hexane solutions at temperatures close to −80°C. in a stream of dry purified argon. The initial monomer was thoroughly freed from traces of moisture by drying over sodium sulfate, purified on 4 A. pore molecular sieves and subsequently distilled, to separate the fraction boiling at 97.3–97.5°C., 752–754 mm. Hg being taken.

There is a lower limit of catalyst concentration, below which no solid crystalline polymer will form, the only product being an amorphous polymer. When the concentration of butyllithium is raised from 0.007 to 0.0109 mole/l. the yield of crystalline polymer increases from 4.5 to 17.6% of the initial monomer (Fig. 1).

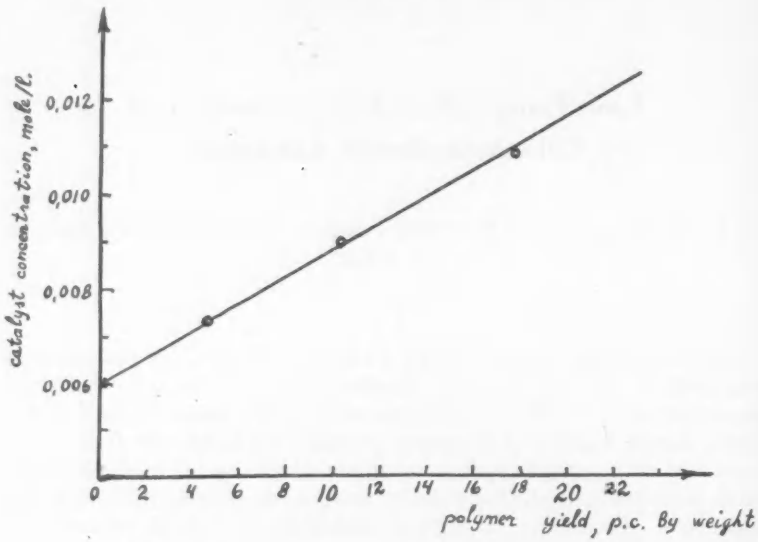


Fig. 1. Effect of catalyst concentration on polymer yield.

Increasing the polymerization reaction time also strongly affects the polymer yield. When trichloroacetaldehyde is polymerized for 5 hr. the polymer yield is 10%, but if the reaction time is increased to 10 hr., other conditions being equal, the polymer yield more than doubles (24.5%).

The polychloral was a white powder of highly crystalline structure, according to the data of x-ray analysis. At room temperature polychloral dissolves in pyridine and is partially soluble in dimethylformamide and methyl ethyl ketone. Neither at room temperature nor when heated to 50°C. will the polymer dissolve in other solvents (dioxane, carbon tetrachloride, hexane, chloro-benzene, tetrahydrofuran, hexachlorobutadiene).

Thermomechanical and thermographic studies (Figs. 2 and 3) show that polychloral is characterized by a melting point of 140°C. and a creep point of above 200°C.

The infrared absorption spectrum of polytrichloroacetaldehyde obtained with a NaCl prism (Fig. 4) reveals a number of bands characterizing the structural elements of the polymer.

The 795, 1070, and 1128 cm.$^{-1}$ bands are characteristic of the C—Cl valence vibrations of the $CCCl_3$ groups; the 664 cm.$^{-1}$ band is also attributed to the C—Cl valence vibrations, and the 822 and 838 cm.$^{-1}$ bands are assigned to the C—Cl bond in the polymer molecule.[4] The intense 963 and 1091 cm.$^{-1}$ bonds are related respectively to the symmetrical and antisymmetrical C—O—C valence vibrations. The 1330 and 1360 cm.$^{-1}$ bands characterize the C—H deformation vibrations.

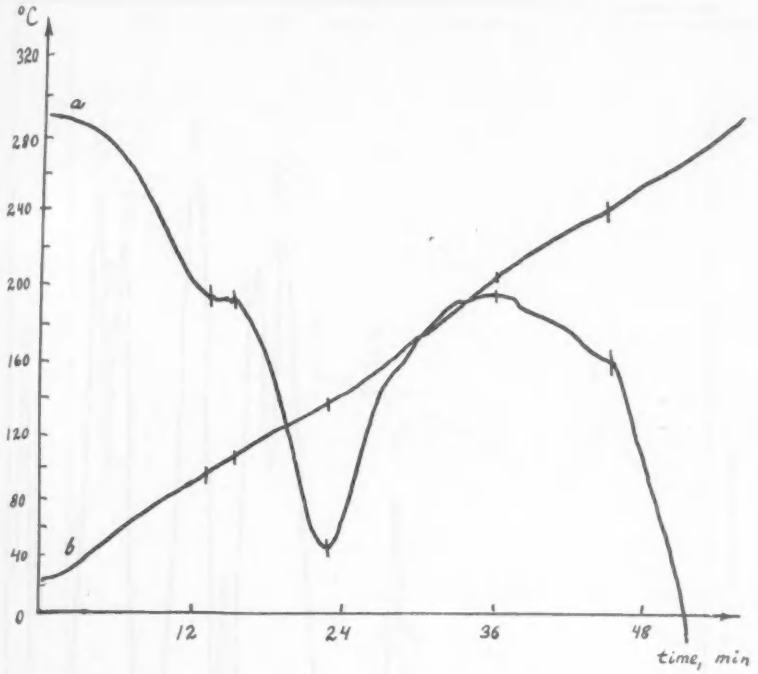


Fig. 2. Thermogram of polychloral: (*a*) simple recording; (*b*) differential recording.

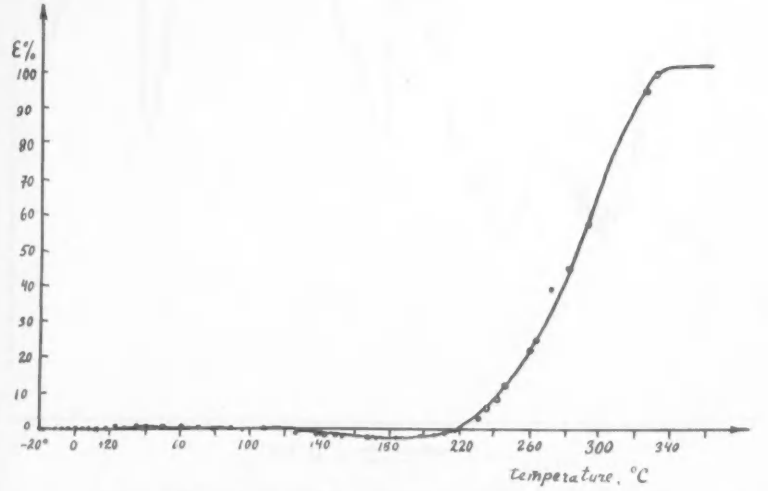


Fig. 3. Thermomechanical curve of polychloral (deformation ε vs. temperature).

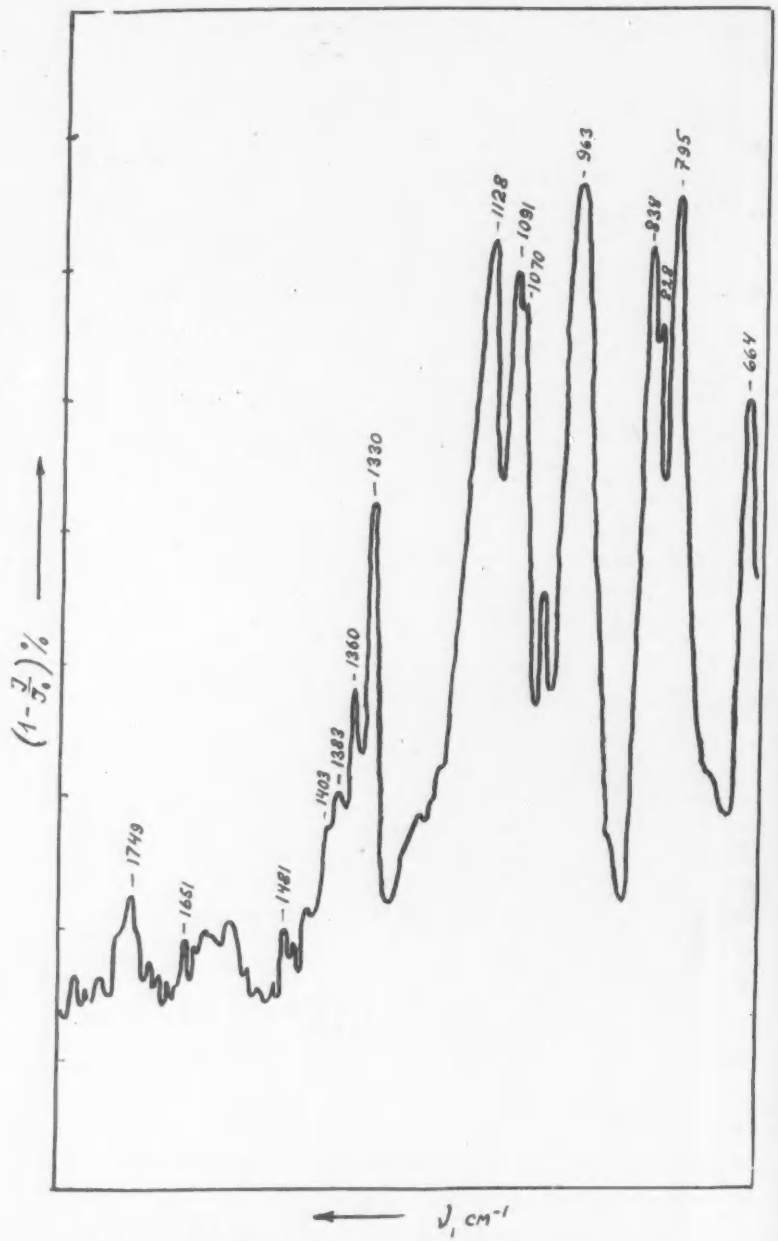


Fig. 4. Infrared absorption spectrum of polychloral (NaCl prism).

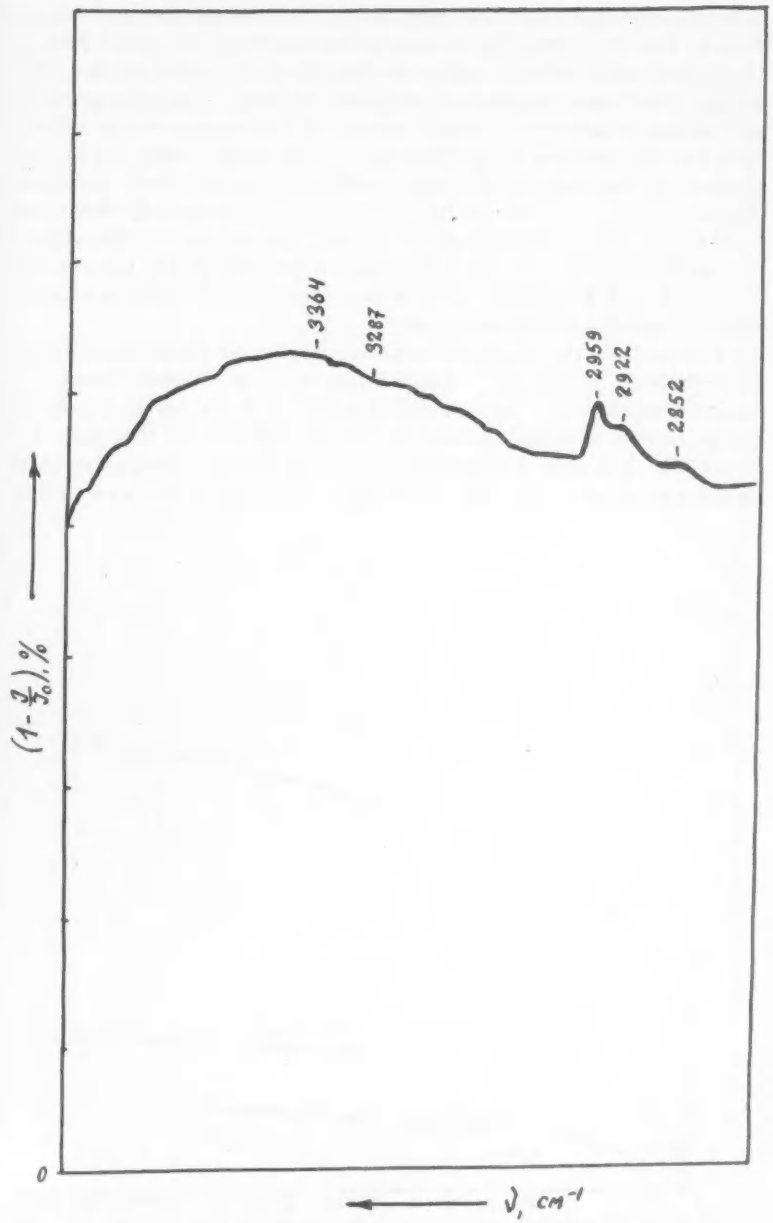


Fig. 5. Infrared absorption spectrum of polychloral (lithium fluoride prism).

In the infrared absorption spectrum of polychloral obtained with a lithium fluoride prism (Fig. 5) a wide band is observed with a peak at about 3364 cm.$^{-1}$ which is related to the valence vibrations of the —OH groups which form complexes by hydrogen bonding. The presence in the polychloral structure of a small amount of OH group, clearly evident from the low intensity of the 3364 cm.$^{-1}$ band, is obviously due to their location at the ends of the large polytrichloroacetaldehyde molecules. The C—H valence vibrations in the CH_3 and CH_2 groups are represented by the 2852, 2922, and 2959 cm.$^{-1}$ bands. The presence in the polymer of a small number of CH_3 and CH_2 groups is probably due to the fact that the CH_3 CH_2 group formed upon decomposition of butyllithium attaches itself to the end of the polymer chain.

Of interest are the results obtained in studying the thermal destruction of polychloral in vacuum.[7] The polymer was heated under vacuum at various temperatures. As is evident from Figure 6, the degree of polymer decomposition increases considerably as the temperature rises from 115 to 208°C. The rate of decomposition of the product remains constant only for 5–15 min., then falls off sharply. For each of the selected tem-

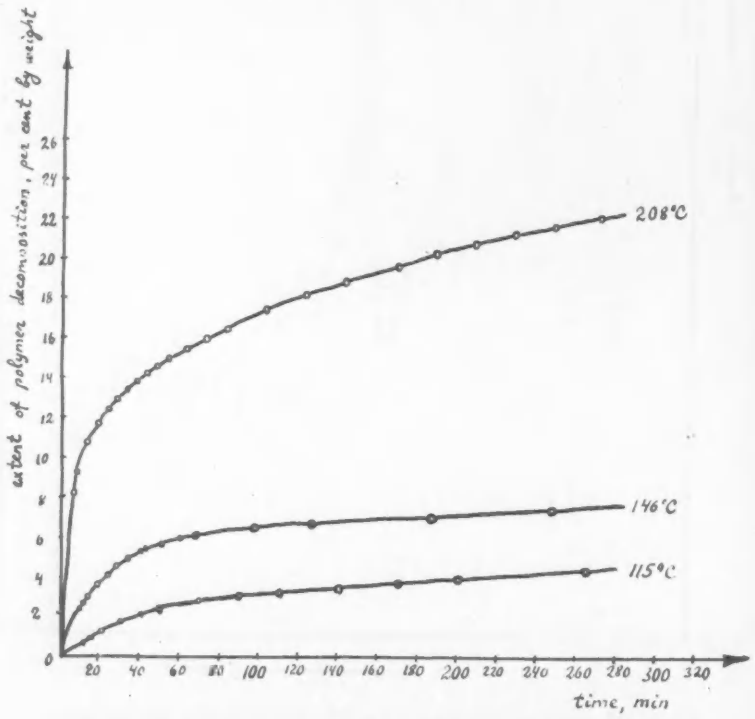


Fig. 6. Effect of temperature on extent of polychloral decomposition.

peratures a "decomposition limit" is observed. Such regularities are not observed in the thermal destruction of other polyaldehydes.

The results obtained give grounds to assume that thermal decomposition involves two processes: (1) destruction of the polymer chains and (2)

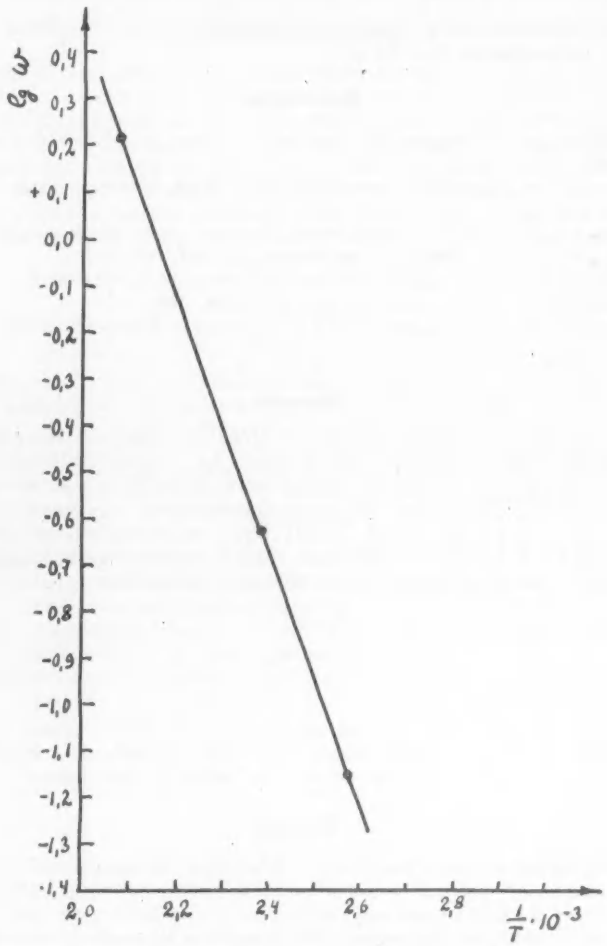


Fig. 7. Temperature vs. initial reaction rate w.

their subsequent relinking, which accounts for the temperature "decomposition limits."

On the basis of the experimental data the initial rates of polymer decomposition and the activation energy E of this process were calculated (Fig. 7). which equals 12.5 kcal./mole.

The value obtained for the activation energy (E = 12.5 kcal./mole) suggests an ionic mechanism of destruction of polytrichloroacetaldehyde.

At present work is being continued on the polymerization of trichloroacetaldehyde and other chloroderivatives of aldehydes and the investigation of their properties.

The authors express their gratitude to N. A. Nechitailo and M. V. Shishkina for their assistance in investigating the polymer.

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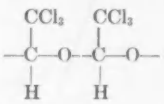
Synopsis

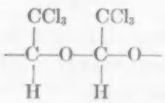
Low temperature polymerization of aldehyde is one of the most promising methods for obtaining stereoregular polymers of the polyether type. Among aldehydes which can be polymerized by this method, our attention was attracted by chlorosubstituted aldehydes containing chlorine atoms with a large inductive effect. An example of such a monomer is trichloroacetaldehyde (chloral), which we polymerized on nucleophilic catalysts at low temperatures. This polymerization proceeds readily at the position of the carbonyl bonds and forms a polymer having the structure:



This polymer is a solid white substance softening at above 220°C.; it was crystalline, as indicated by x-ray diffraction studies. The infrared spectra show that there are alkyl radicals and hydroxyl groups at the ends of macromolecular chains.

Résumé

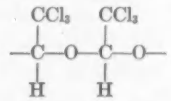
La polymérisation à basse température de l'aldéhyde est une des méthodes la plus prometteuse en vue d'obtenir des polymères stéréoréguliers du type polyéther. Parmi les aldéhydes qui peuvent être polymérisés par cette méthode, notre attention a été attirée par les aldéhydes chlorosubstitués contenant des atomes de chlore possédant un grand effet d'induction. Comme exemple d'un tel monomère, nous pouvons mentionner le trichloracétaldéhyde (chloral), que nous avons polymérisé avec des catalyseurs nucléophiles à basse températures. La polymérisation commence rapidement à l'endroit des liaisons carbonyles et forme le polymère suivant



Ce polymère est une substance solide blanche ayant un point de ramollissement situé au-dessus de 220°C. Il diffracte les rayons-X, ce qui est une caractéristique d'une substance cristalline. L'analyse des spectres infra-rouges montre qu'il y a des radicaux alcoyles et des groupes hydroxyles à la fin des chaînes macromoléculaires. A l'heure actuelle nous étudions la réaction de polymérisation du trichloroacétaldéhyde et d'autres aldéhydes chlorosubstituées.

Zusammenfassung

Die Tieftemperaturpolymerisation von Aldehyden ist eine der aussichtsreichsten Methoden, um stereoreguläre Polymere vom Polyäthertyp zu erhalten. Unter den Aldehyden, die nach dieser Methode polymerisiert werden können, verdienen die chlorsubstituierten Aldehyde wegen des grossen induktiven Effekts der Chloratome besondere Aufmerksamkeit. Als Beispiel eines solchen Monomeren sei Trichloracetaldehyd (Chloral) erwähnt, der mit nukleophilten Katalysaoren bei tiefer Temperatur polymerisiert wurde. Diese Polymerisation erfolgt leicht an der Carbonylbindung unter Bildung des folgenden Polymeren:



Dieses Polymere ist eine feste weisse Substanz mit einem Erweichungspunkt oberhalb 220°C. Es liefert ein für eine kristalline Substanz charakteristisches Röntgendiagramm. Sein Infrarotspektrum zeigt die Anwesenheit von Alkylradikalen und Hydroxylgruppen an den Kettenenden der Makromoleküle. Gegenwärtig wird die Polymerisationsreaktion von Trichloracetaldehyd und anderen chlorsubstituierten Aldehyden untersucht.

Discussion

Y. Tabata (*University of Tokyo, Japan*): I would like to comment about the polymerization of chloral. We have also studied the polymerization of chloral by high energy initiation. The polymerization is possible in the liquid and in the solid phase by ionizing radiation. The activation energy is about 7 kcal./mol. in the liquid phase at low temperature. In the solid state, the rate of polymerization is much faster than in liquid. We believe that in the liquid phase, the polymerization proceeds by an ionic mechanism.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1009–1026

Polymerization of Nitriles and Pyridine

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INTRODUCTION

During the last few years there has been considerable interest in preparation of polymers with conjugated double bonds containing nitrogen atoms in the chain. The conventional methods used for this purpose include polycondensation or secondary reactions in polymer chains (cyclization, reactions with elimination of small molecules, etc.). The direct routes for synthesis of such compounds would be polymerization of nitriles at the C≡N bond and ring-opening polymerization of aromatic nitrogen-containing heterocyclics. However the estimation of free energies of these polymerizations indicates that no polymerization reaction can occur under the conditions typical for polymerization of vinyl or acetylenic compounds. This is explained by the fact that estimated heat of polymerization at the C≡N bond even if one takes resonance energy into account cannot be substantially more than zero. As the entropy of polymerization of R—C≡N compounds is negative, the conversion nRCN → [—RC=N—]$_n$ will be followed with an increase of free energy of the system. The stability of aromatic heterocycles to the ring-opening polymerization is apparently related to loss of resonance energy of the cycle which at ordinary temperature is not balanced by the probable positive entropy of the reaction. This means that the "floor" temperature of polymerization of these cyclic compounds must be too high, probably higher than the temperature of chemical degradation.

The present paper describes some results on polymerization of nitriles and nitrogen-containing heterocyclics in stoichiometric complexes with some metal halides. In these systems complex formation causes a change in the free energy of polymerization and also provides some kinetic advantages for the reaction.[1–4]

EXPERIMENTAL*

Monomers used were benzonitrile, capronitrile, propionitrile, and pyridine. All the monomers were carefully purified in accordance with accepted techniques[5] and except for pyridine were additionally dried over cal-

* Some of the experiments were carried out by I. P. Terekhina, D. A. Topchiev, and E. T. Zakharenco.

cium hydride. The constants of purified monomers coincided with the literature data.

The following complexes with $ZnCl_2$, BF_3, $TiCl_4$ were used for polymerization: $(C_6H_5CN)_2 \cdot TiCl_4$, $(C_6H_5CN)_2 \cdot ZnCl_2$, $C_6H_5CN \cdot BF_3$, $(C_6H_{11}CN) \cdot TiCl_4$, $(C_5H_{11}CN_2) \cdot ZnCl_2$, and $(C_5H_5N)_2 \cdot ZnCl_2$.

Pure zinc chloride was dried *in vacuo* at 180°C. for 5–6 hr. before preparation of the complexes. Titanium tetrachloride was purified by repeated vacuum distillations. Boron trifluoride was obtained just before preparation of the complex by thermal decomposition of phenyldiazonium boron fluoride.[6]

Infrared spectra were obtained with a NKC-14 double-beam infrared spectrophotometer. The samples were prepared by the KBr pellet technique.

Complexes were obtained by mixing stoichiometric quantities of monomer and complexing agent in complete absence of atmospheric moisture. Polymerization was carried out in sealed ampules evacuated to high vacuum (10^{-5} mm. Hg) and kept in thermostat at temperatures of 150–250°C. in the case of nitriles and at 330–390°C. in case of pyridine. In some experiments anhydrous metaphosphoric acid (0.5–6 wt.-%) was used as an initiator.

After the reaction the ampules were opened and products of the reaction were reprecipitated from sulfuric acid solutions by water. The inorganic substances were proved to remain in solution. The precipitate containing the polymerization products was washed with aqueous ammonia, then with distilled water and was dried to the constant weight.

NITRILES

Studies of Structure of Polymerization Products

Heating of nitrile complexes under different reaction conditions leads to formation of two types of products. The first one involves black high polymers (having an intrinsic viscosity in concentrated H_2SO_4 of 0.05–0.2), and the second involves practically colorless substances of lower molecular weight.

The elementary analysis data and the molecular weights as determined by cryoscopic measurements in benzene indicate that the latter are trimers of nitriles. For example, for benzonitrile calculated values for C_7H_5N C were 81.56%, N 13.59%, H 4.88%; values found were C 81.46%, N 13.54%, H 4.90%. Molecular weight calculated for $(C_6H_5CN)_3$ is 309, found 314. For capronitrile ($C_6H_{11}N$) calculated values were C 74.2%, N 14.4%, H 11.35%; analysis yielded found values of C 73.5%, N 12.8%, H 11.35%. Molecular weight calculated for $(C_5H_{11}CN)_3$ is 291, found 288.

To ascertain the structure of the polymerization products the infrared spectra of the monomers, trimers, and polymers of benzonitrile, propionitrile, and capronitrile were studied. Figure 1 shows infrared spectra of benzonitrile and the products of its polymerization.

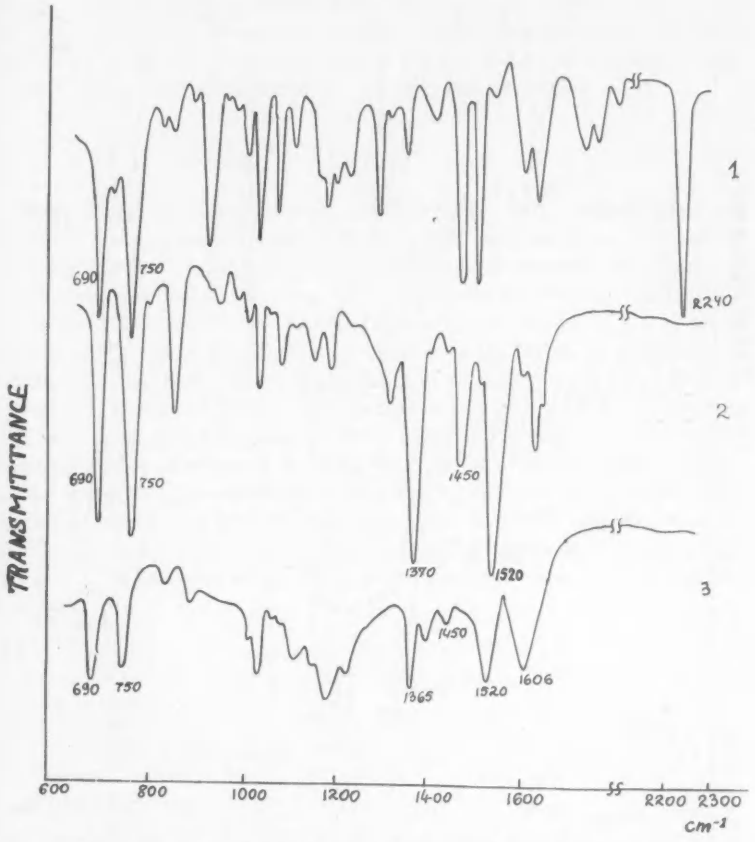


Fig. 1. Infrared spectra of benzonitrile and its polymerization products: (*1*) benzonitrile; (*2*) trimer; (*3*) polymer.

A comparison of the spectra of monomer (curve *1*, Fig. 1), and trimer (curve 2, Fig. 1) shows that in the trimer spectrum the peak corresponding to the C≡N bond (2240 cm.$^{-1}$) has disappeared. An intense band at 1520 cm.$^{-1}$ corresponding to substituted triazene ring vibrations has appeared. According to the infrared-spectrum and some properties the trimer was assigned the structure of *sym*-triphenyltriazene (cyaphenin). This compound is often formed on treatment of benzonitrile with various acidic agents.[7]

The spectrum of high polymer (curve *3*, Fig. 1) obtained by heating of the $(C_6H_5CN)_2 \cdot TiCl_4$ complex at 250°C. shows all main modes typical for trimer (bands at 750 and 690 cm.$^{-1}$ which correspond to nonplanar bending modes of monosubstituted benzene rings). There is also a new intense band at 1606 cm.$^{-1}$ probably corresponding to conjugated C=N bond in linear

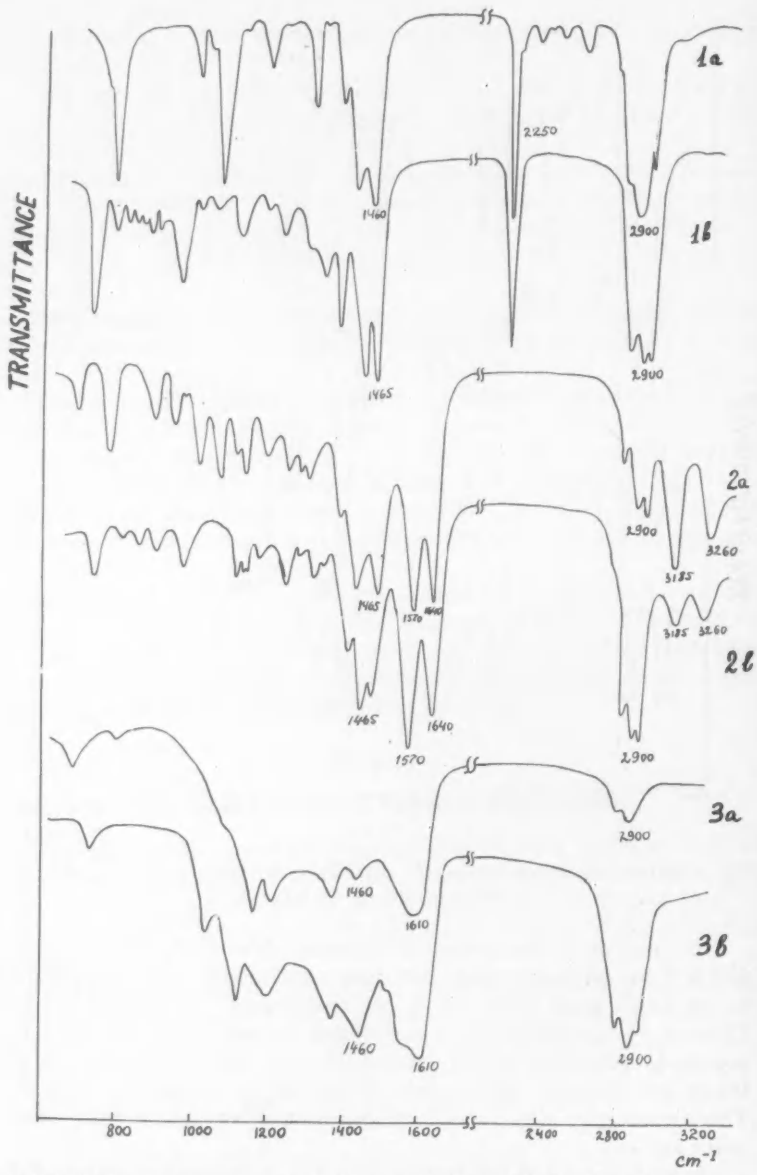
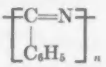
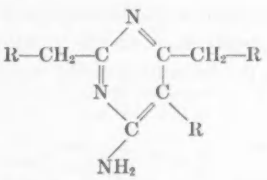


Fig. 2. Infrared spectra of propionitrile, capronitrile, and their polymerization products: (*1a*) propionitrile; (*1b*) capronitrile; (*2a*) trimer of propionitrile; (*2b*) trimer of capronitrile; (*3a*) polypropionitrile; (*3b*) polycapronitrile.

chain. This apparently means that conversion of benzonitrile to high polymer proceeds on the polymerization of C≡N bonds and is not accompanied by noticeable decomposition of phenyl groups of monomer molecules.* Hence the structure of the polymer can be written as†



The infrared spectra of trimers and polymers of aliphatic nitriles (propionitrile and capronitrile) were also compared with spectra of the corresponding monomers (Fig. 2). The polymers were prepared by heating of $ZnCl_2$ complexes at 250°C. and $TiCl_4$ complexes at 200°C. Comparison of the spectra of monomeric nitriles (curves *1a* and *1b*, Fig. 2) with those of trimers (curves *2a* and *2b*, Fig. 2) shows that the latter, as in the case of benzonitrile, do not contain a nitrile band at 2250 cm.$^{-1}$ Two intense peaks at 1640 and 1570 cm.$^{-1}$ which can be attributed to the pyrimidine ring vibrations and two peaks of lower intensity at 3260 and 3185 cm.$^{-1}$ which probably correspond to associated primary amino groups appear. At the same time, the bands corresponding to the stretching vibrations of aliphatic C—H bonds at 2960–2850 cm.$^{-1}$ and bands at 1465 cm.$^{-1}$ corresponding to deformational vibrations in aliphatic groups remain almost unchanged. On the basis of this the trimers were given the aminopyrimidine structure:



Products of this type are often formed on treatment of aliphatic nitriles with acidic reagents.[7] The ultraviolet spectrum of the propionitrile trimer also confirms the proposed structure. It has two maxima at 230 and 270 mμ and coincides with the ultraviolet spectra of similar aminopyrimidines.[8]

In spectra of polymers of propionitrile and capronitrile (curves *3a* and *3b*, Fig. 2) as well as in spectra of trimers, the absorption band of the nitrile group (2250 cm.$^{-1}$) is absent, and there is a broad, intense band at 1600–1620 cm.$^{-1}$ apparently corresponding to C=N conjugated bonds in linear chain. The peaks at 2960–2860 cm.$^{-1}$ and at 1460 cm.$^{-1}$ which correspond to the modes of aliphatic groups remain. However, in the polymer spectra the peaks at 3260 and 3180 cm.$^{-1}$ which are present in spectra of trimers are absent. On the basis of this it was concluded that the polymers are formed

* The stability of phenyl groups under the reaction conditions was demonstrated by prolonged heating of benzene with large quantities $TiCl_3$ at 350°C.

† The heating of triphenyltriazene with H_2O + $CuCl_2$ + $AlCl_3$ catalyst[14] which converts benzene into black polyphenyl was not followed with polymer formation.

by the polymerization of the C≡N bond without degradation of side alkyl groups. And thus the structure of polymers may be written as

$$\left[\begin{array}{c} -C=N- \\ | \\ C_nH_{2n+1} \end{array}\right]_x$$

Higher temperature polymerization (300°C., complexes with $ZnCl_2$) leads to formation of two-phase system (polymer and a mobile liquid which is shown by gas chromatography to be a mixture of cracking products of alkyl side groups. As expected, the spectrum of such a polymer does not contain the C—H stretching model band at 2960–2850 cm.$^{-1}$

Mechanism of Polymerization of Nitriles

To elucidate the mechanism of polymerization of nitriles the kinetics of polymerization of benzonitrile complexed with titanium tetrachloride was studied. It was found that in all experiments trimer was formed as well as polymer, and the rate of polymerization and the polymer–trimer ratio was dependent on temperature and the presence of small amounts of proton-donating compound (acids, water, etc.) and small amounts of some other promotors in the system. Therefore the rate of formation of reaction products as a function of temperature and concentration of initiator (solid HPO_3) was studied.

The kinetic results are shown in Figures 3–6. The rate of polymerization increases with temperature and concentration of the initiator. The polymer yield increases with time but the yield of trimer goes through a maximum being high at the beginning of the reaction and then decreasing

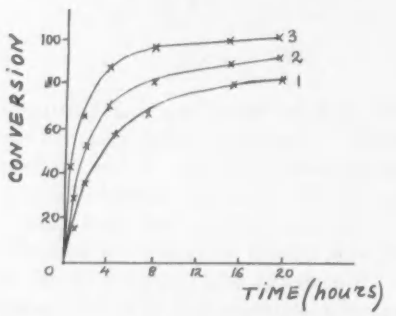


Fig. 3. The degree of conversion in the polymerization of the benzonitrile–$TiCl_4$ complex as a function of time at 250°C.: (*1*) without initiator; (*2*) 1 wt.-% HPO_3, (*3*) 6 wt-% HPO_3.

practically to zero. This indicates that trimer is one of the intermediate products which, along with monomer, disappears during the reaction. At fixed time of polymerization, the amount of trimer decreases with an increase of temperature and concentration of initiator.

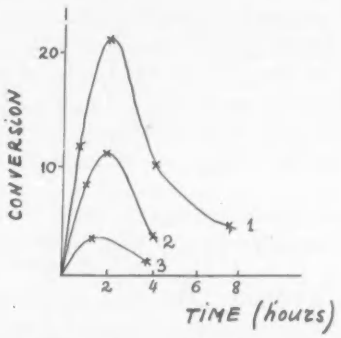


Fig. 4. Accumulation and disappearance of triphenyltriazene in benzonitrile polymerization at 250°C.: (*1*) without initiator; (*2*) 1 wt.-% HPO_3; (*3*) 6 wt.-% HPO_3.

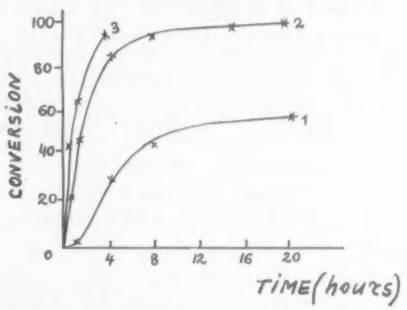


Fig. 5. The degree of conversion in the polymerization of benzonitrile–$TiCl_4$ complex as a function of time at concentration of HPO_3 of 6 wt.-%: (*1*) 200°C.; (*2*) 250°C.; (*3*) 300°C.

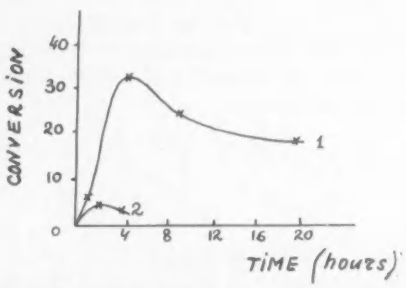


Fig. 6. Accumulation and disappearance of trimer in the polymerization of benzonitrile at a concentration of HPO_3 of 6 wt.-%: (*1*) 200°C.; (*2*) 250°C.

However figures 3 and 4 show that polymerization can proceed without added initiator. This may be related to the presence in the system of traces of water, HCl, etc. To check this possibility a few experiments were carried out with particularly careful purification of monomer and $TiCl_4$ with-

out any contact with atmospheric moisture at all stages of the experiment. The complex was prepared *in vacuo* in an all-sealed glass apparatus. In this case polymerization also proceeded and yields of polymers in two parallel runs. (4 hr. polymerization at 250°C.) were 47% and 46% compared with 53% obtained with the usual technique. This means that the polymerization of benzonitrile–$TiCl_4$ complex probably can proceed without proton initiator.

The polymerization of benzonitrile complexed with some less active acceptors (BF_3, $ZnCl_2$) was carried out. After heating the benzonitrile–boron trifluoride complex for 10 hr. at 250, 275, and 300°C. only trimer with the traces of polymer was formed. The same result was obtained with the benzonitrile–zinc chloride complex. In both cases polymerization with added initiator leads to formation of polymer.

The results of these experiments can be explained by with the following mechanism.* In presence of initiator the chain may be started by the proton acid which can be formed at the reaction of metal halide with proton compound (e.g. HPO_3).

1. Initiation:

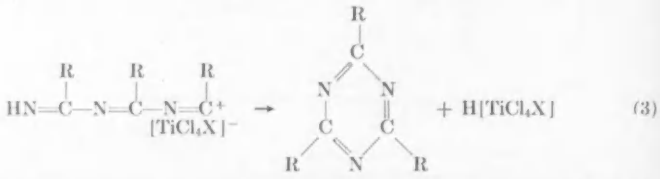
$$\mathrm{R{-}C{\equiv}N{:}TiCl_4 + HX \rightarrow R{-}C{\equiv}N + H^+[TiCl_4X]^-}$$

$$\mathrm{\underset{H^+[TiCl_4X]^-}{\overset{R}{\overset{|}{N{\equiv}C}}} \rightarrow \underset{[TiCl_4X]^-}{\overset{R}{\overset{|}{HN{=}C^+}}}} \qquad (1)$$

2. Propagation:

$$\mathrm{\underset{[TiCl_4X]^-}{\overset{R}{\overset{|}{HN{=}C^+}}} + \underset{TiCl_4}{\overset{R}{\overset{|}{N{\equiv}C}}} \rightarrow \underset{TiCl_4\quad [TiCl_4X]^-}{\overset{R\qquad R}{\overset{|\qquad|}{HN{=}C{-}N{=}C^+}}} \quad \text{etc.} \qquad (2)}$$

The formation and accumulation of the trimer at the earlier stages of the reaction can be explained by assuming that after the third step of chain propagation, parallel with further propagation, there appears an opportunity for ring closure with the formation of a stable, six-membered ring and regeneration of the proton initiator:



$$\mathrm{+ H[TiCl_4X]} \qquad (3)$$

This results in formation and accumulation of trimer as a less active product in the system (Figs. 5 and 6). In the later stages of the reaction, as benzonitrile disappears, the rate of formation of trimer becomes less than its rate of polymerization and the amount of trimer in the system decreases.

* The second monomer molecule in the complex is not shown in this mechanism scheme R in this scheme is C_6H_5.

The trimer disappearance is due to its ring-opening polymerization as it was shown by heating of trimer–$TiCl_4$ complex which results in formation of the polymer having infrared spectrum similar to curve (*3*) of Figure 1.

Lower activity of the trimer in polymerization is probably connected with the higher activation energy of the ring-opening reaction in comparison with the reaction of C≡N groups according to the eqs. (1) or (2). The decrease of maximum trimer yield at higher temperatures confirms this assumption (Fig. 5).

The polymerization of aliphatic nitriles may be complicated with the participation of active α hydrogen atoms in the reaction (e.g., in initiation). The proof of this may be the fact that isomerization with the formation of pyrimidine derivatives takes place on trimerization of these nitriles.

PYRIDINE

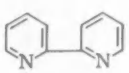
Heating pyridine–zinc chloride complex ($ZnCl_2 \cdot Py_2$) in the same way as nitriles results in formation of dark colored products. In absence of proton initiator the reaction proceeds at an appreciable rate only at temperatures higher than 380°C. Prolonged heating at temperatures below 380°C. does not cause any perceptible chemical changes in the complex. However the addition of anhydrous HPO_3 to the system allows the reaction to be carried out at considerably lower temperatures. The reaction is not followed by the formation of gaseous products. Marked chemical degradation occurs only at higher temperatures (above 400°C.).

It was proposed that polymerization of the pyridine–$ZnCl_2$ complex proceeds by a ring-opening reaction with the formation of polymer $(—CH=CH—CH=CH—CH=N—)_n$. In order to prove this the infrared spectra of two specially synthesized compounds:

O=CH—CH=CH—CH=CH—N=CH—CH=CH—CH=CH—OH

(I)

and



(II)

were compared with the corresponding spectrum of polymer.[9,10]

The spectrum of dipyridyl (II) (Fig. 7) contains double band with two sharp maxima at 1550 and 1590 cm.$^{-1}$ which correspond to the pyridine ring modes. The spectra of polypyridine and compound I have, instead, a broad, intense band with a maximum at 1600 cm.$^{-1}$ which probably corresponds to conjugated double bonds in the linear chain. The spectra of these products also do not have a band at 755 cm.$^{-1}$ corresponding to deformational vibrations of C—H bonds in pyridine rings. All this is in favor of the idea that polymerization of pyridine is really a ring-opening reaction. The

formation of a system of condensed pyridine rings must also be followed by evolution of gaseous products (mainly H_2), but when the polymerization was carried out at 370°C. and at lower temperatures there was no gas evolution.

Typical kinetic curves for polymerization of pyridine are shown in Figure 8. The rate of reaction increases with time. The intrinsic viscosity of polymer solutions in sulfuric acid changes in the same way. Intrinsic viscosities of polymers did not change after reprecipitation from sulfuric acid.

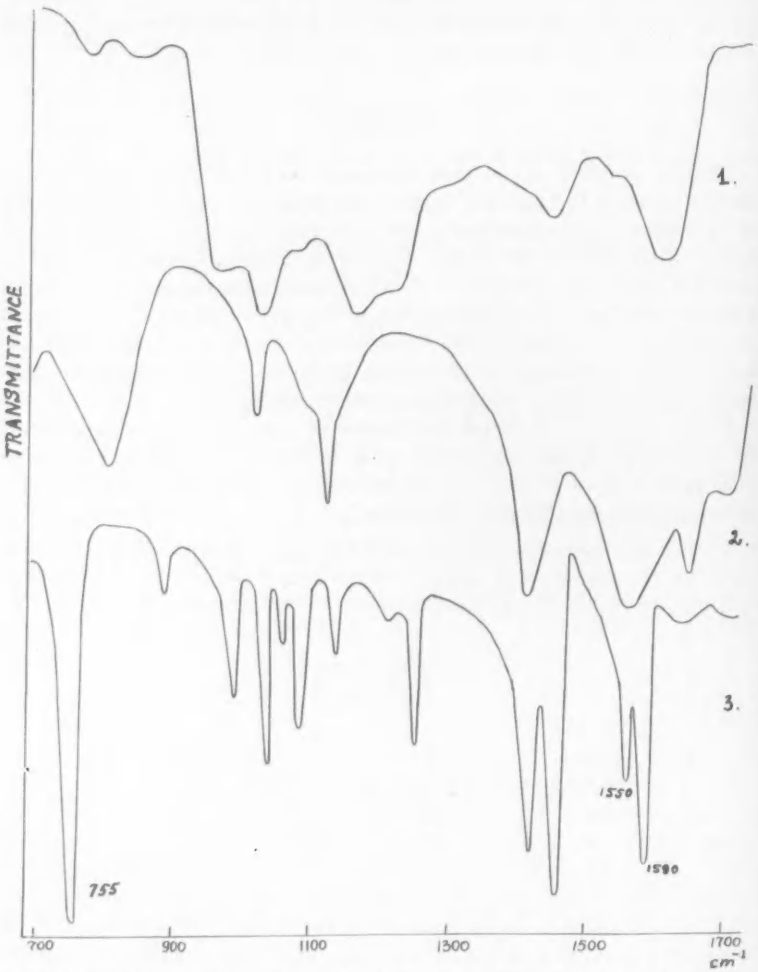


Fig. 7. Infrared spectra of pyridine and model compounds I and II: (*1*) polypyridine; (*2*) model compound I; (*3*) model compound II.

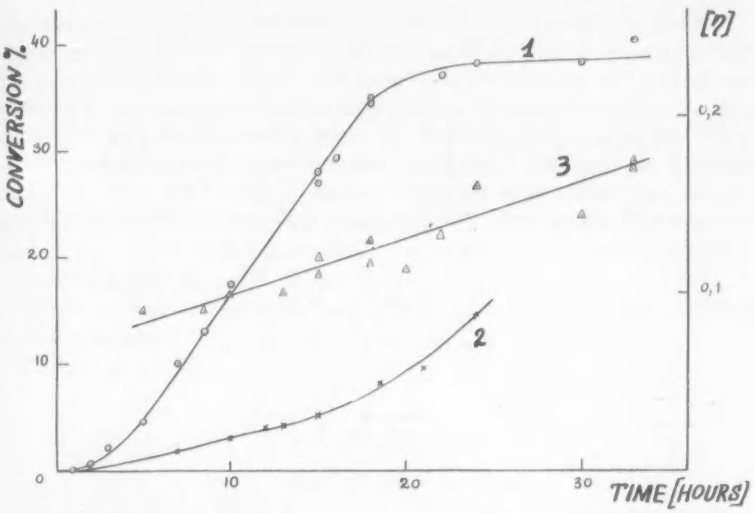


Fig. 8. Plots of (*1*), (*2*) degree of conversion and (*3*) intrinsic viscosity of polymers as functions of time in the polymerization of the pyridine–$ZnCl_2$ complex: (*1*) conversion at 350°C.; (*2*) conversion at 330°C.; (*3*) intrinsic viscosity in the H_2SO_4 (350 polymerization).

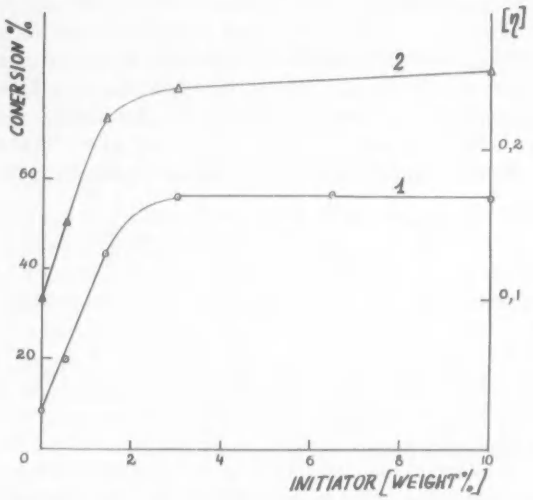


Fig. 9. Plots of (*1*) degree of conversion and (*2*) intrinsic viscosity as functions of HPO_3 concentration in the polymerization of the pyridine–$ZnCl_2$ complex at 390°C., polymerization time 10 hr.

In Figure 9 conversion and intrinsic viscosities of the polymers are plotted as functions of initiator (HPO_3) concentration at constant time of polymerization. It can be seen that degree of conversion and intrinsic viscosity increase with concentration of initiator. The whole set of these facts could hardly be explained in terms of usual polymerization kinetics. The proposed mechanism is based on the assumption of the autocatalysis of the reaction by conjugated polymer molecules formed.[2,11] The simplest scheme of an autocatalytic reaction of this type can be written as follows.

1. Initiation:

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{A}$$

$$\mathrm{I} + \mathrm{M} + \mathrm{P} \xrightarrow{k_i} \mathrm{A}' + \mathrm{P}$$

2. Propagation:

$$\mathrm{A}_n + \mathrm{M} \xrightarrow{k_p} \mathrm{A}_{n+1}$$

$$\mathrm{A}_n' + \mathrm{M} \xrightarrow{k_p'} \mathrm{A}_{n+1}'$$

3. Termination:

$$\mathrm{A}_n + \mathrm{M} \xrightarrow{k_t} \mathrm{P}_{n+1}$$

$$A_n' + \mathrm{M} \xrightarrow{k_t'} \mathrm{P}_{n+1}$$

where I is initiator, M is monomer, P is a unit of preformed polymer chain, A is an active chain in monomer medium, A′ is an active chain in contact with preformed polymer chain (the same symbols will be used to designate the concentrations), k_i, k_i', k_p, k_p', k_t, and k_t' are rate constants for initiation, propagation, and termination with active centers A and A′. The termination step is assumed to be first-order, as was assumed for radiation-induced polymerization of phenylacetylene.[12] The kinetic equations are formally identical to those derived by Kargin et. al.[13] The steadystate treatment and integration gives for degree of conversion Q

$$Q = \frac{M_0 - M}{M_0} = \frac{e^{\alpha I_0(1+\delta)t} - 1}{e^{\alpha I_0(1+\delta)} + \delta} \tag{4}$$

and for weight-average degree of polymerization (P_w) of polymer formed in the interval of time t, $(t + dt)$:

$$P_w = \left[\frac{e^{\alpha I_0(1+\delta)t} + \delta}{(1+\delta)e^{\alpha I_0(1+\delta)t}}\right]\frac{k_p}{k_t} + \left[\frac{(e^{\alpha I_0(1+\delta)t} - 1)\delta}{(1+\delta)e^{\alpha I_0(1+\delta)t}}\right]\frac{k_p'}{k_t'} \tag{5}$$

where M^0 is the initial monomer concentration, and

$$\alpha = k_p k_i / k_t$$

$$\beta = k_p' k_i' / k_t'$$

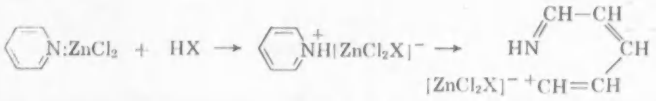
$$\delta = \beta M_0 / \alpha$$

and I_0 is concentration of initiator. (The integration was carried out under the assumption that the concentration of initiator changes negligibly during the reaction).

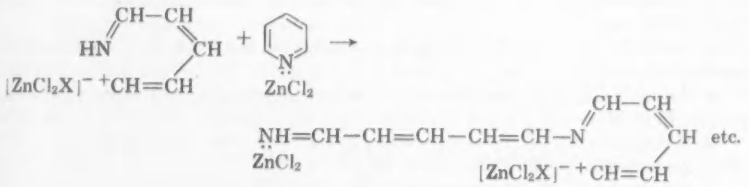
If $\delta > 1$ the reaction is autocatalytic. The value of δ shows how much the rate of polymerization increases when active chains are in contact with preformed polymer molecules or their aggregates. It is easy to see that eqs. (4) and (5) predict the increase of rate and degree of polymerization with the time of reaction and increase of degree of polymerization with concentration of initiator at fixed time of polymerization. Treatment of kinetic curve I (Fig. 8) gives $\delta \simeq 10$.

The probable chemical mechanism of polymerization of pyridene may be written as follows:

1. Initiation:



2. Propagation:



Adsorption of growing chain or the initiator–monomer complex on the polyconjugated molecule may result in increase of initiation and propagation constants. The mechanism of termination requires further study.

THERMODYNAMICS OF POLYMERIZATION

Finally the question of thermodynamics of polymerization of nitriles and pyridine as a reaction with the shift of chemical equilibrium is briefly discussed. The heat of polymerization of C≡N bonds is not higher than zero. However when a stoichiometric quantity of complexing agent is added to the system the total heat of polymerization will comprise the difference of heats of formation of complexes with initial and final products. Nitrogen atoms in polyconjugated polymer chains are probably more basic than those in nitrile groups of the monomer. Therefore complex formation with polymer products results in a decrease of enthalpy of the system and brings about a shift of equilibrium to the direction of formation of polymeric products. However, it was shown that parallel with formation of the polymer formation and accumulation of the trimer was observed which, however, disappeared later when the ring-opening polymerization reaction commenced. The same type of ring-opening polymerization was realized

in the case of pyridine. The transition from the unstrained aromatic ring to a linear conjugated chain cannot be exothermal. Even in the presence of complexing agent, it is probably endothermic. The role of the complexing agent in such a polymerization reaction might be to reduce the resonance energy in aromatic rings of triazene or pyridine owing to the complex formation. This may decrease the endothermal character of the reaction. In addition, the complexing agent is a plasticizer for the polymer chains and thus increases the entropy of the final state and ΔS of polymerization. When appreciable amounts of the polymer are formed in the system, the heat of reaction may be changed on account of heat of interaction of polyconjugated chains or heat of their aggregation. It may be that this factor may be the decisive one in shifting the cycle–polymer equilibrium to the formation of the polymer.

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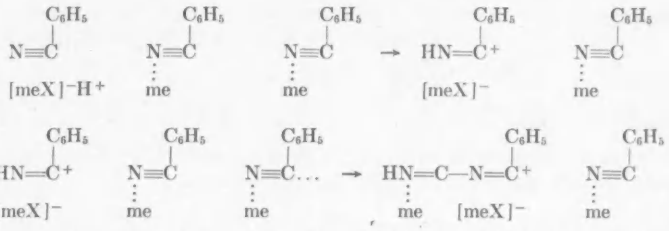
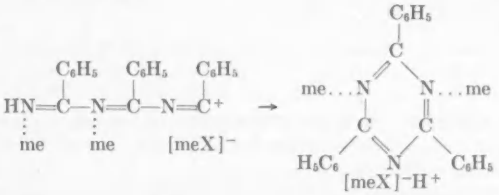
Synopsis

The polymerization of some nitriles (acetonitrile, propionitrile, capronitrile, benzonitrile) was carried out in stoicheometric complexes with $TiCl_4$, $ZnCl_2$, and BF_3. The structure of the products prepared was studied by infrared spectroscopy. It was suggested that the polymerization proceeded through C≡N bonds and gave resulting polymer with conjugated bonds in chains. The mechanism of the reaction was studied in the systems $2C_6H_5CN \cdot TiC_2$, $2C_6H_5CN \cdot ZnC_2$, and $C_2H_5CN \cdot BF_3$. It was found that at the initial stages of polymerization cyclic trimer of benzonitrile was also formed and then polymerized through opening six-membered ring. The initiators of polymerizations were proton-containing substances (e.g., H_3PO_4, HPO_3). The proposed polymerization mechanism implied the following sequence for initiation and propagation:



At the step of formation of trimer there are two possibilities. The first one is cyclization with regeneration of initiator:



and the second one is an addition of the next nitrile molecule and further chain propagation. The rate of polymerization and rates of accumulation and disappearance of trimer depended on temperature and concentration of proton initiators. The possibility of polymerization of pyridine in melted stoichiometric complexes of the types $ZnCl_2 \cdot Py_2$, $TiCl_4 \cdot Py_2$ was also shown. The infrared spectra of polymerization products and spectra of specially synthesized model compounds indicate that polymerization of pyridine consisted in ring-opening and formation of chains of the structure:

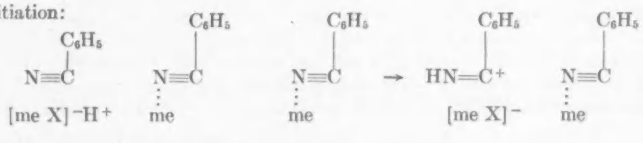
$$[CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}N{=}]_n$$

The rate of polymerization and molecular weight of products increased with time of the reaction. The initiators of polymerization were the same proton donors as in the case of nitriles. The molecular weight of polymers increased with increasing initiator concentration. An attempt was made to explain the results obtained on the basis of the autocatalytic character of growth of polymer chains.

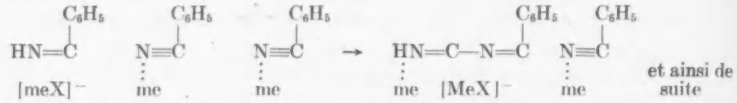
Résumé

On a réalisé la polymérisation de quelques nitriles (acétonitrile, propionitrile, capronitrile, benzonitrile) en complexes stoéchiométriqies avec $TiCl_4$, $ZnCl_2$, BF_3. On a étudié au moyen de la spectroscopie infra-rouge la structure des produits préparés. On prouve que la polymérisation procède par liens C≡N et donne un polymère avec des liens conjugués dans la chaîne. On a étudié le mécanisme de la réaction en employant les systèmes 2 $C_6H_5CN \cdot TiCl_4$, 2 $C_6H_5CN \cdot ZnCl_2$, $C_2H_5CN \cdot BF_3$. On a trouvé qu'à l'état initial de la polymérisation un trimère cyclique du benzonitrile se formait aussi et polymérisait alors par cycle ouvert à six membres. Les initiateurs de polymérisation sont des substances contenant des protons (par exemple H_3PO_4, HPO_3). Le mécanisme de polymérisation proposé implique:

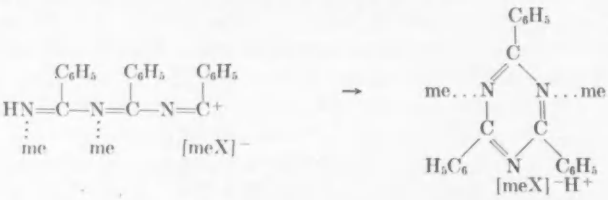
(1) Initiation:



(2) Propagation:



Pour l'étape de formation du trimère il y a deux possibilités: la première possibilité est une cyclisation réversible avec régénération de l'initiateur



et la seconde possibilité est une addition de la molécule de nitrile voisine et propagation ultérieure de la chaîne. La vitesse de polymérisation et les vitesses d'accumulation et de disparition du trimère dépendent de la température et de la concentration en protons initiateurs. On montre aussi la possibilité de polymérisation de la pyridine dans des complexes stoéchiométriques de $ZnCl_2 \cdot Py_2$, $TiCl_4 \cdot Py_2$. Les spectres infra-rouges des produits de polymérisation et les spectres de composés modèles spécialement synthétisés prouvent que la polymérisation de la pyridine consiste dans l'ouverture de cycles et dans la formation de chaînes de structure suivante:

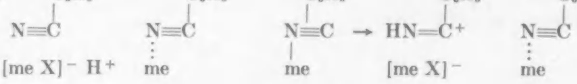
$$[-CH{=}CH-CH{=}CH-CH{=}CH-N{=}]_n$$

On a prouvé que la vitesse de polymérisation et le poids moléculaire des produits augmentent au cours de la réaction. Les initiateurs de polymérisation sont les mêmes donneurs de protons que dans le cas des nitriles. Le poids moléculaire des polymères augmente avec l'augmentation de la concentration en initiateur. On explique les résultats obtenus sur la base du caractère autocatalytique due chaîne de polymère en croissance.

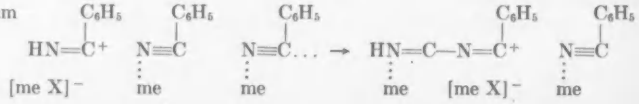
Zusammenfassung

Die Polymerisation einiger Nitrile (Acetonitril, Propionitril, Capronitril, Benzonitril) in stöchiometrischen Komplexen mit $TiCl_4$, $ZnCl_2$, BF_3 wurde durchgeführt. Die Struktur der dargestellten Stoffe wurde infrarotspektroskopisch untersucht. Es wurde gezeigt, dass die Polymerisation über die C≡N-Gruppe verläuft und Polymere mit konjugierten Doppelbindungen in der Kette liefert. Der Reaktionsmechanismus wurde an den Systemen $2C_6H_5CN \cdot TiCl_4$, $2C_6H_5CN \cdot ZnCl_2$ und $C_2H_5C \cdot NBF_3$ untersucht. Es wurde gefunden, dass im Anfangsstadium der Polymerisation auch ein cyclisches Trimeres des Benzonitrils gebildet wurde, das dann durch Öffnung des sechsgliedrigen Ringes weiterpolymerisierte. Die Polymerisation wurde durch protonen-hältige Substanzen (z.B. H_3PO_4, HPO_3) gestartet. Folgender Polymerisationsmechanismus wird vorgeschlagen:

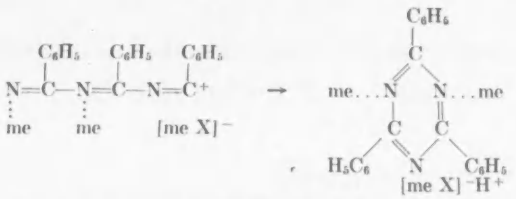
(1) Start



(2) Wachstum



und so weiter. Auf der Stufe des Trimeren bestehen zwei Möglichkeiten. Die erste ist die reversible Cyclisierung unter Rückbildung des Starters:



und die zweite eine Addition des nächsten Nitrilmoleküls und weiteres Kettenwachstum. Die Polymerisationsgeschwindigkeit und die Bildungs- und Verbrauchsgeschwindigkeit des Trimeren hängen von Temperatur und Konzentration des Protonenstarters ab. Auch die Möglichkeit der Polymerisation von Pyridin in den geschmolzenen stöchiometrischen Komplexen $ZnCl_2 \cdot Py_2$ und $TiCl_4 \cdot Py_2$ wurde nachgewiesen. Die Infrarotspektren der Polymerisationsprodukte und Spektren von eigens synthetisierten Modellverbindungen bestätigen, dass die Polymerisation des Pyridins in einer Öffnung der Ringe und Bildung von Ketten der folgenden Struktur:

$$[=CH—CH=CH—CH=CH—N=]_n$$

besteht. Es stellte sich heraus, dass Polymerisationsgeschwindigkeit und Molekulargewicht der Produkte mit der Reaktionsdauer zunehmen. Als Starter dienten die gleichen Protonendonatoren wie im Falle der Nitrile. Das Molekulargewicht der Polymeren nahm mit steigender Starterkonzentration zu. Es wurde versucht, die Ergebnisse unter Annahme eines autokatalytischen Charakters des Wachstums der Polymerketten zu erklären.

Discussion

J. W. Breitenbach (*Vienne, Austria*): You have described the polymerization of nitrile and pyridine in your complex system. Obviously the conjugated double bonds in the nitrile polymer are stable under your reaction conditions. This seems remarkable to me and I wonder if you ever have tried to polymerize simple compounds with C—N-double bonds in your complex system.

V. A. Kabanov: No, we didn't try to do that.

W. H. Calkins (*du Pont de Nemours, Wilmington, Del.*): What were the molecular weights achieved in the chloralpolymers?

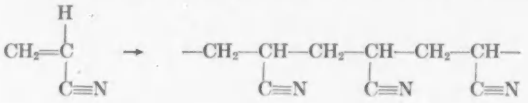
V. A. Kabanov: We do not know the relationship between the $[\eta]$ and the molecular weight. So I cannot give the exact values. We suppose that the degree of polymerization is not higher than 20–30.

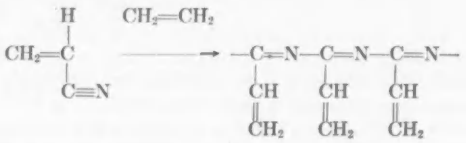
J. B. Rosset (*Rhodiacéta, Lyon, France*): Avez-vous étudié les propriétés semiconductrices des polyméres que vous avez obtenus?

V. A. Kabanov: We did not do this specially. We studied some usual electrical properties (activation energy of conductivity, for example) only to characterize the polymers synthetized.

Y. Tabata (*University of Tokyo, Japan*): This paper is quite interesting for us. We have also some data about the polymerization of nitriles. We have studied the polymerization of acrylonitrile and alkylnitriles in ethylene solutions by high energy initiation. It was observed that the rate of polymerization gradually decreases with the concentration of ethylene and exhibits a minimum for about equimolar concentrations. Thereafter the rate increases with the concentration of ethylene. The structure of the polymers obtained was analyzed by the infrared method. It was concluded from these results that the polymerization mainly occurs via the C=C double bond in the region of

high concentrations of acrylonitrile and via the C≡N triple bond in the region of dilute concentrations of the monomer. The structure of the polymer obtained is as follows





In the case alkylnitriles, we also observed a very similar phenomenon.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1027–1041

Mechanochemical Reactions of Polymerization and Degradation at Low Temperatures

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In studying solid-state polymerization–a process which is characterized by several kinetic and thermodynamic particularities[1]–the radiation method of initiation usually is used. This is done due to the great penetrating capacity of irradiation when one works with organic crystals. Another not so widespread but extremely effective method of initiation is the chemical one involving a joint evaporation and successive condensation of monomer and catalyst vapors on a cooled surface *in vacuo*.[2] In fact, these two methods are practically the only ones used in studying the process of solid-state polymerization.

In a study of the reactivity of freshly formed surface of inorganic substances[3–6] we found that intense mechanical disintegration of solid salts and oxides results not only in the polymerization of liquid monomers but is able to initiate the polymerization of monomers below their melting points.[7] The initiation of this type of polymerization is connected with the fact that during the mechanical disintegration of particles of quartz (SiO_2), TiO_2, graphite, etc., rupture of covalent bonds is taking place, and radical-type active centers on the surface of these particles are created. These active centers may interact with surrounding monomer molecules, which results in the polymerization. The disintegration of such compounds as NaCl, $BaSO_4$, CaF_2, etc. results in formation of structural flaws in ionic-type lattice like F-centers which can ionize themselves with electron emission.[5,6] In the presence of monomer molecules this process also initiates the ion-radical type polymerization. Not entering into details of the mechanism of initiation in systems studied by us[6] it should be pointed out that these polymerization processes are very effective in absence of usual initiators and catalysts.

In this paper the possibility of application of mechanochemical initiation for studying the polymerization of monomers below their melting point, i.e. in the solid state, is discussed. This method of polymerization may expand the basic experimental approaches for studying the solid-state polymerization and brings to light several interesting peculiarities of this process.

Experimental Methods

Monomers used for investigation were: methacrylamide (MAA), m.p. 104°C., acrylamide (AA), m.p. 84°C., and methyl methacrylate (MMA), m.p. −50°C. All monomers were purified by classical methods directly before the polymerization.

Ionic salts (NaCl, $BaSO_4$) as well as quartz powder (SiO_2) were purified also.

Monomer together with catalyst was subjected to intense mechanical treatment in a vibration apparatus in which the dispersion of monomer and catalyst crystals was taking place. The process of disintegration was carried out either under an inert gas in steel hermetic glasses which contained steel balls or in vacuum in glass ampules with glass balls. In first case the excentric vibration mill[4] was used, while in the second case a specially designed electromagnetic vibrator[6] was employed. The working frequency of both type of apparatus was 50 cycles/sec. and the amplitude varied from 2 to 5 mm.

The degree of conversion was an experimentally determined value which was estimated after the dissolution of the reaction mixture in hot water or acetone. Both solvents contained hydroquinone as a stabilizer to prevent or to minimize side-effects, which may be connected with the possible polymerization of monomers during the melting process.

The maintenance of constant temperature during the polymerization was achieved by permanent immersion of the glass ampule attached to vibrator into a Dewar flask or into a thermostating bath with a suitable liquid as contents. In the case of the steel vibration mill the disintegration was carried out in glasses with water cooling or in glasses which were periodically immersed into the liquid nitrogen. In the last case the experiment was accomplished by short periods of 30 sec. with temperature control by means of a sensitive thermocouple introduced into the steel glass.

Results Obtained and Discussion

Figure 1 shows the yield of polymethacrylamide (PMAA) as a function of the duration of disintegration in the vibromill in the presence of 0.5% NaCl at 20°C. After a short induction period the polymerization rate increases and then reaches a constant value. If one compares the efficiency of the vibromill and the electromagnetic vibrator it may be concluded that vibromill is the more effective; disintegration of a MAA–NaCl mixture (1 wt.-% NaCl) for 6 hrs. in the vibrator results in a degree of conversion only 2.9%, MAA while in the vibromill the degree of conversion is 10% after 50 min.

The polymerization efficiency is sharply affected by variation in monomer/catalyst ratio. In the Fig. 2 the yield of PMAA is plotted against the NaCl/MAA and $BaSO_4$/MAA ratio (duration of reaction is 45 min. at 20°C). The polymerization begins already when the content of NaCl in the system is 0.005%, and at 0.5% NaCl the degree of conversion is maximal.

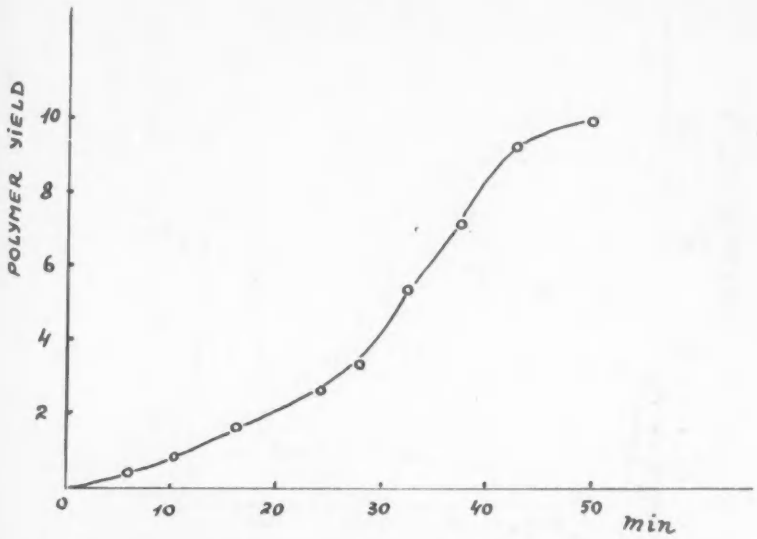

Fig. 1. Kinetics of mechanochemical polymerization of methacrylamide at 20°C. in the presence of 0.5% NaCl.

The reaction curves for $BaSO_4$ and NaCl are exactly the same, which indicates a common mechanism. In the case of crystalline quartz the process is analogous (Fig. 3), but with sharper maximum of conversion at 5% contents of SiO_2.

The reaction products are not only high molecular weight compounds but also oligomers of MAA. Molecular weight determination by a cryoscopic method showed that these were dimers and trimers of MAA. Figures 2 and 3 show the ratio between high molecular fraction and oligomers at different contents of catalyst in the systems.

Some results obtained in this field are summarized in Table I. From these data it can be shown that at all ratios of monomer and catalyst the

TABLE I
Polymerization of MAA

NaCl content, %	$[\eta]$ of PMAA fraction[a]	Molecular weight of oligomers
0.5	0.145	256[b]
5.0	0.148	244[b]
10.0	0.150	172[c]
20.0	0.150	168[c]

[a] In water at 18°C.
[b] MW of trimer MAA = 255.
[c] MW of dimer MAA = 170.

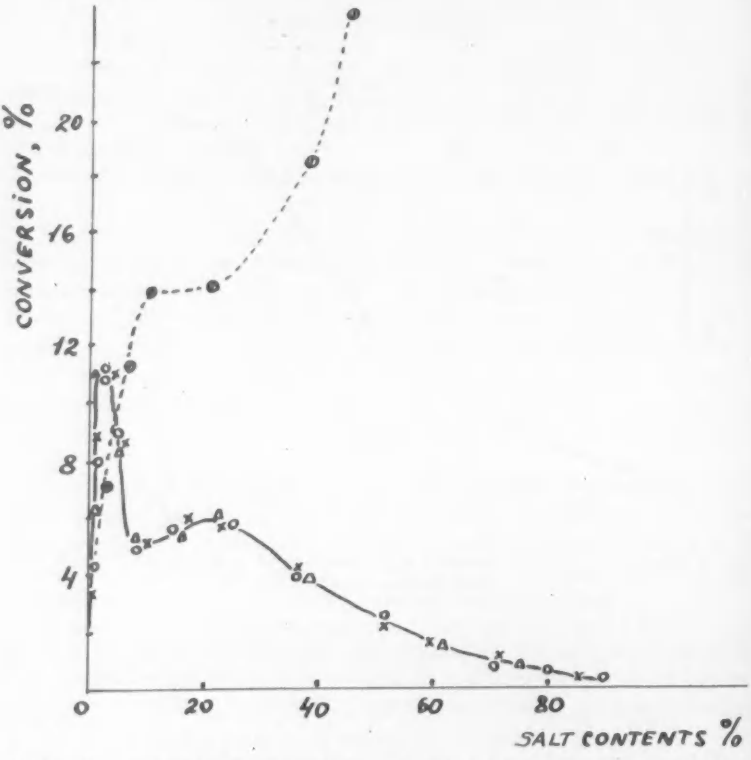

Fig. 2. Conversion of methacrylamide at various MAA/catalyst ratios: (○) NaCl–MAA; (×) $BaSO_4$–MAA; (△) NaCl–MAA–heptane; (⊖) oligomers of MAA in the presence of NaCl. Grinding time 45 min.

products of reaction are polymethacrylamide with intrinsic viscosity of 0.15, and trimers and dimers of MAA. The reasons for this phenomenon will be discussed later.

To elucidate the role of phase state of MAA in the mechanochemical polymerization of MAA experiments were carried out with disintegration of $BaSO_4$ and SiO_2 in water and NaCl and $BaSO_4$ in benzene solutions of MAA at 20°C. In none of these cases was polymerization observed. At the same time, the addition of an inert diluent like heptane into the NaCl–MAA system does not influence the polymerization efficiency (Fig. 2). Results obtained show the important role of the crystalline state of MAA as a necessary condition for this mechanochemical-initiated polymerization process.

Acrylamide, as is shown in Table II, can also be polymerized under the same conditions at room temperature and to a greater extent below this temperature. From the data in Table II it may be concluded that investi-

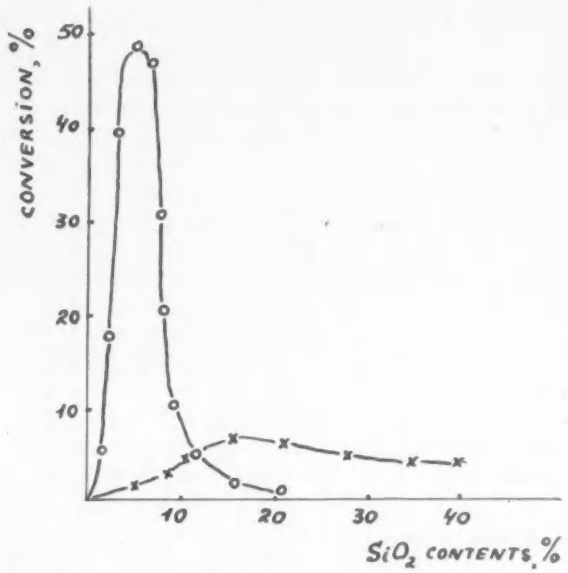

Fig. 3. Mechanochemical polymerization of MAA with SiO_2: (O) polymethacrylamide; (×) oligomers of MAA.

gated monomers can be polymerized mechanochemically in the presence of NaCl at the temperatures which are 220–270°C. lower than the respective melting points. It should be noticed that several authors[9–11] indicate that these monomers do not polymerize at all at temperatures below −70°C.

Methyl methacrylate, as seen from Table II polymerizes as well in the liquid state (we have been shown this earlier[6]) as in the crystalline state. In the latter case, i.e., at −65 and −190°C. (melting point of MMA is −50°C.), the degree of conversion is lower. In other words, methyl methacrylate does not represent an exception among monomers and can be polymerized in solid state under the conditions of mechanochemical synthesis.

The mechanism of initiation in mechanical disintegration of solid ionic-type salts like NaCl or $BaSO_4$,[4–6] includes the formation of an ion-radical from the monomer molecule due to the joining of electron from the catalyst. The ionic salt can be a source of electrons, as shown by electron spin resonance[8] if it is subjected to vibrational mechanical forces. The ionization of flaws like F-centers occurs and the anion-radical formed

$$CH_2{=}CHR + \bar{e} \rightarrow \overset{\ominus}{C}H_2{-}CHR\cdot$$

may react with other monomer molecules at both reactive ends. Without going into the details of propagation reaction and taking into account of the sharp decrease of polymerization rate of MAA in the presence of 0.5% hy-

TABLE II
Polymerization of MAA, AA, and MMA at various temperatures with NaCl

Monomer	NaCl, wt.-%	Vibration apparatus type	Grinding time, min.	Temp., °C.	Conversion to polymer, %	[η] of Polymer	Molecular weight of polymer[a]
Methacrylamide	0.5	Vibromill	45	20	10.4	0.155[b]	
					10.6		
					10.3		
"	0.5	"	45	−110	6.1		
					6.3	0.172[b]	
Acrylamide	1	Electromagnetic vibrator	360	20	10.8	6.4[c]	2.5×10^6
					10.2		
					10.5		
"	1	" "	360	−65	7.4		
					6.05	6.1[c]	2.4×10^6
					6.3		
"	1	" "	360	−190	0.8		
					1.2		
					0.9		
Methyl methacrylate	1	Electromagnetic vibrator	360	20	4.7		
					4.7		
					4.5		
" "	1	" "	360	−65	0.7		
					0.8		
					0.7		
" "	1	" "	360	−190	0.5		
					0.4		
					0.5		

[a] Calculated from[9] $[\eta] = 3.73 \times 10^{-4} M^{0.66}$.
[b] In water at 18°C.
[c] In water at 30°C.

droquinone the suggestion can be made, that polymerization proceeds through a radical mechanism. This suggestion is confirmed by the fact that the same type of curves are obtained for the NaCl–MAA, $BaSO_4$–MAA and SiO_2–MAA systems, and in the last case the existence of radical-type centers on the fresh surface of quartz was experimentally proved by an ESR method[8].

The specificity of initiation in the heterogenous system in question lies in the transfer of active center from one solid phase to another, from NaCl or SiO_2 to monomer. To elucidate features of the propagation reaction in mechanochemical synthesis under heterogenous conditions, experiments were made on the copolymerization of acylamide and methyl methacrylate at three different temperatures when the systems are in different phase states. The results obtained are summarized in Table III, in which are given the copolymer composition at three temperatures and equivalent values of relative activities r_1 and r_2 calculated following Mayo-Lewis equation. Phase analysis of systems AA–MMA studied showed that this

TABLE III
Copolymerization of AA and MMA at Various Temperatures

Temperature, °C.	Conditions of copolymerization	Initial ratio AA:MMA (weight)	N (Kjeldahl) in copolymer, (wt.-%)	Copolymer composition AA:MMA (weight)	Relative reactivity ratios	
					r_1	r_2
70	Solvent benzene, 0.15% AIBN; homogeneous system	20:80	12.1	62:38	4.2	0.12
		30:70	13.8	71:2		
20	Without solvent; 1% NaCl; crystal–liquid	10:90	0.6	3:97	7.5	7.0
		30:70	4.5	23:77		
−65	Without solvent; 1% NaCl; crystal–crystal	20:80	8.5	43:57	36.6	4.2
		40:60	16.1	82:18		

is a one-phase homogenous system at 70°C.; at 20°C. there occurs the crystallization of AA and the system becomes a heterogenous one of the crystal–liquid type; at −65°C. there is a mixture of two types of crystals MMA and AA which does give neither a solid solution nor eutectic. As one can see from Table III, the equivalent values r_1 and r_2 calculated as hypothetic values supposing the validity of reactivity theory in homogenous systems there is an increase in rate of attack of a radical on its "own" monomer with decreasing temperature

$$r_1 = k_{AA-AA}/k_{AA-MMA}$$

$$r_2 = k_{MMA-MMA}/k_{MMA-AA}$$

This means that the more the system becomes more heterogenous in case of exfoliated monomers the more polymerization proceeds independently inside each phase. Generally, a system containing two monomers which can easily copolymerize with another under homogenous conditions tends to independent homopolymerization of both monomers resulting in the formation of mixture of two polymeric substances from different monomers. This represents a very rare case in homogenous copolymerization. The appearance of a boundary between the two crystalline phases makes difficult growing chain transfer from one monomer to another. Thus phase heterogeneity of the monomer system strongly affects on the character of the polymerization process in solid state.

The fact itself of polymerization of several crystalline monomers at temperature far below the melting point is not usual. In some cases, the polymerization temperature is as much as 270°C. below melting point of the monomer (for example for acrylamide polymerization at −190°C.). Such a mechanochemical polymerization is closely connected with the ordered state of molecules in crystalline lattice and not with a local increase of temperature at the moment of breaking of monomer and catalyst particles by grinding balls. This is proved by the fact that polymerization of MAA does not take place in solution in spite of generation of active centers in case of NaCl, $BaSO_4$, and SiO_2 when polymerization of other liquid monomers occurs. The fact of polymerization of acrylamide in glass ampules at liquid nitrogen temperature (−190°C.) and at acetone–Dry Ice temperature (−65°C.), i.e., in conditions under which heat generation is practically negligible because of blows of balls confirm the suggestion above mentioned. Thus taking into account the overall picture, that is, polymerization process which develops in solid state of monomer with rates much higher than in the case of radiation polymerization of same monomers,[9,10] we believe that such a difference in polymerization rates is due to the peculiarities of mechanochemical synthesis. As has been shown in some papers dealing with solid-state radiation polymerization,[11,12] the reaction starts from the surface of monomer crystals in flaws and develops on the crystal–polymer boundary, where the stress which arises inevitably when the polymer chain grows is at a minimum. The contraction during polymerization creates always new flaws which can become traps for growing radicals. The removal and curing of flaws as well as stress relaxation–processes which are slowed down in static crystals of monomers far from the melting temperature– are really possible when one realizes the intensive mechanical grinding of crystals.[7]

In fact, during continuous mechanical grinding of crystals the molecules of renovated surface layer can be mobile enough for getting over the stress and flaws which are created by growing chains, and in such a system conditions of combined ordered state and high mobility are achieved. This situation is analagous to the situation which appears at phase transitions and which results in explosive polymerization of monomers in solid state.[2] These conditions, together with the continuous generation of active cen-

ters, leads to the rapid polymerization of acrylamide and methacrylamide in the solid state.

These ideas are confirmed by results on the mechanochemical polymerization of crystalline salts of acrylic acid, which is realized due to electron defects in the ionic lattice of the monomer in absence of additional sources of initiation.[5] It was shown for this system (studied in details in our previous work[13]) that vibrational grinding of potassium and sodium acrylate leads to the polymerization of the latter. The rate of such polymerization increases when small quantities of ethanol are added to the system. Ethanol contributes to the loosening of surface layers in the ionic-type lattice which is stronger than the molecular-type lattice of acrylamide or methacrylamide (Fig. 4).

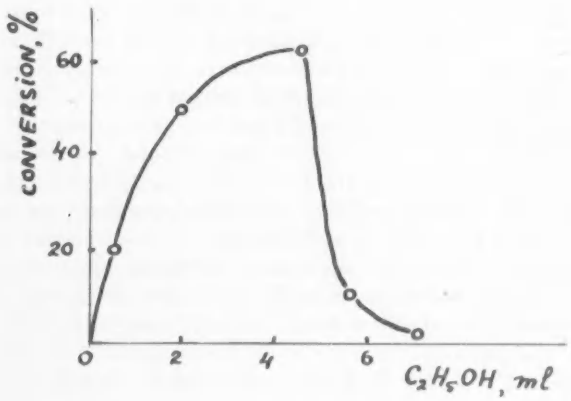

Fig. 4. Mechanochemical polymerization of potassium acrylate in the presence of ethanol at 20° C.

If the considerations above about the reasons of fast polymerization reactions under mechanical grinding of crystals are valid, then the polymerization rate and consequently the yield of polymer at a given time must not essentially depend on temperature if the efficiency of grinding itself and of initiation remains constant. Really, as can be seen from Table II, in case of MAA a decrease in temperature of about 130°C. (from 20 to −110°C.) results in a decrease of polymer yield of only 1.6-fold. In the case of AA, a decrease in temperature of 85°C. lowers the polymer yield 1.5 times, and a change in temperature of 210°C. lowers the yield only 10 times. If one calculates the approximate value of total activation energy of polymerization, a value of 0.4–0.7 kcal./mole can be obtained for these systems as well as for polymerization of methyl methacrylate in solid state. Thus the specific use of mechanical energy from outside results in lowering of activation energy, and polymerization of these monomers in the solid state is characterized by very low values of E_a which are strongly different from

suitable values for homogeneous radical polymerization. According to data reported by Adler[11] for the case of radiation-induced polymerization of acrylamide in solid state under irradiation, E_a is about 3 kcal./mole and 10 kcal./mole for postpolymerization.

Some suggestions can now be made about the character of basic steps in such a polymerization. Molecular weights of polymers of MAA and AA at two different temperatures are practically the same (Table II). This means that the polymer chain is growing at a constant rate, taking into account the above mentioned low value of activation energy determined at two temperatures which differ by 85–130°C. This may be attributed in general either to low activation energy of initiation (if one supposes that propagation and termination rates are equal), or to a low value of the activation energy of the propagation reaction itself. As the total E_a for postpolymerization of acrylamide in the solid state was found equal to + 10 kcal./mole,[11] i.e., the observed E_a for propagation was found to prevail over E_a of the termination step because of zero activation energy of initiation in radiation polymerization, it is difficult to suppose that in our system E_a for termination might reach the value of E_a of the chain propagation reaction. On the contrary, the chain termination process in solid-state polymerization proceeds usually on the structural flaws,[11] the concentration of which does not change with temperature if the conditions of grinding remain constant. This termination reaction is a monomolecular process and can apparently proceed without energy of activation. Therefore the most probable supposition is that the lowering of total activation energy in mechanochemical synthesis in the solid state is due to the lowering of the activation energy of the chain propagation step. A small temperature coefficient may be connected with slight change in efficiency of initiation when temperature decreases.

Thus on continuous renovation of surface of solid monomer by intense mechanical grinding and together with the generation of active centers conditions are created for rapid growth of polymer chains in ordered system practically without activational requirements. The most defect crystalline lattice of monomer and not an ideal crystal is found to be the most reactive in these conditions. The results obtained may be considered as one of experimental proofs of validity of the Semenov hypothesis[1] of the possibility of polymerization processes without activation energy and through energetic chains.

During the mechanochemical polymerization the mechanical degradation of chains formed occurs. It was pointed out above that the process of MAA polymerization leads to the formation of a polymer fraction with same molecular weight and dimers and trimers of methacrylamide. On studying the degradation of pure polymethacrylamide (PMAA) in solid state at +20°C. in the vibromill in the absence of any other substances we have found that products of this degradation process are monomer, dimers, and trimers of MAA as well as polymer of unchanged molecular weight. Some data obtained are summarized in Table IV.

TABLE IV
Composition of Products after Mechanical Degradation of PMAA at 20°C. for 45 min.

Initial polymer	$[\eta]$ of initial polymer[a]	Polymer yield after degradation, wt.-%	$[\eta]$ polymer formed	Oligomer yield, %	Mw of oligomers[b]	Monomer yield, %
PMAA obtained mechanochemically with 0.5% NaCl	0.15	74	0.15	14	257 248	12
PMAA obtained mechanochemically with 5% SiO_2	0.048	88	0.048	10.8	256	1.2
PMAA obtained mechanochemically with 5% SiO_2 + 0.5% NaCl	0.062	94	0.062	6	168	—
"	0.058	93.6	0.057	6	185 154	0.4

[a] In water at +20°C.
[b] By cryoscopic method in benzene.

It can be seen from this table that after the degradation the initial quantity of polymethacrylamide is transformed to the low molecular weight products (trimers, dimers, and monomer) with average yield of about 10% and the polymer of the same intrinsic viscosity. The relatively high content of low molecular weight products and the maintenance of molecular

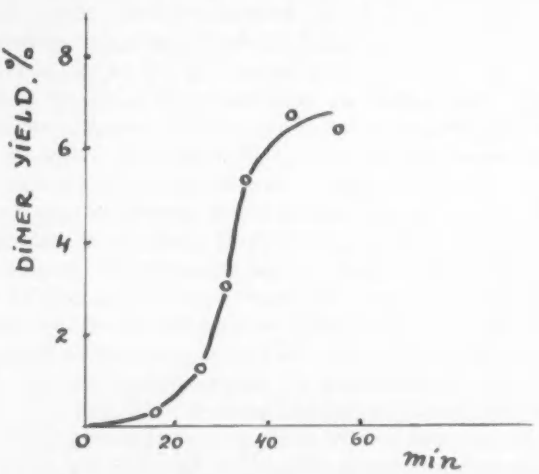

Fig. 5. Mechanical degradation of polymethacrylamide.

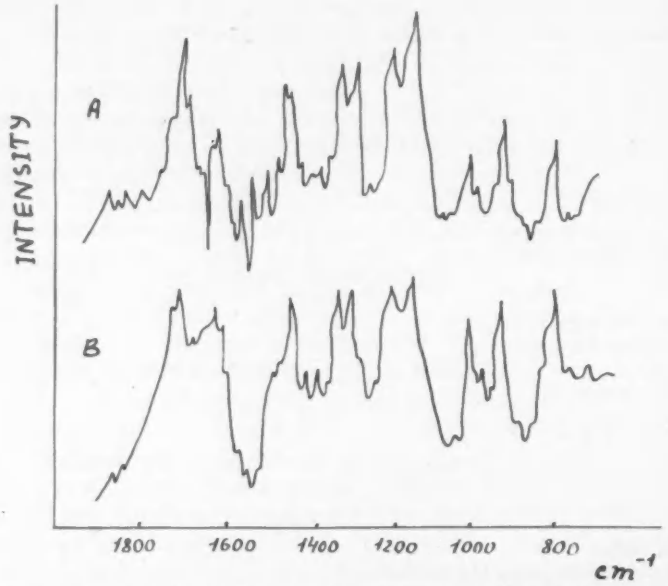

Fig. 6. Infrared spectra of (*A*) methyl methacrylate; (*B*) material under investigation.

weight of polymer remained is not the usual picture of classical mechanical degradation which is accompanied by decrease of total average molecular weight of polymer.[14] The kinetical curve of this unusual degradation process is given in Figure 5.

We have also studied for control the mechanical degradation of polymethyl methacrylate at different temperatures under mechanical grinding in vibromill. It was found that PMMA with average viscometric molecular weight about 5×10^6 after grinding at 25°C. for 45 min. was transformed into polymer having a molecular weight of about 3.3×10^4 without formation of any observed quantities of low molecular weight products. If the same process is carried out at −85°C. it leads to the formation of polymer with $M = 5.5 \times 10^4$, i.e., higher than in the previous case and of some quantity (~10%) of organic liquid which looked like monomeric methyl methacrylate. The isolation of this liquid substance after the degradation was performed in high vacuum by evacuation from the ampule which contained the reaction mixture. This mixture was initially kept at −70°C. for 10 hr. in dry box. The elementary analysis and physical constants showed that this was indeed monomeric methyl methacrylate. Infrared spectra and mass spectra of the product obtained as well as of a control sample of methyl methacrylate are given in Figures 6 and 7, respectively. A comparison of the infrared spectra of these two substances shows that basic bands of absorption corresponding to valent vibrations of C=O groups and C—O groups in esters of nonsaturated acids, which are situated at 1730–1750, 1320–1250, and 1180–1130 cm.$^{-1}$ are markedly observed in both

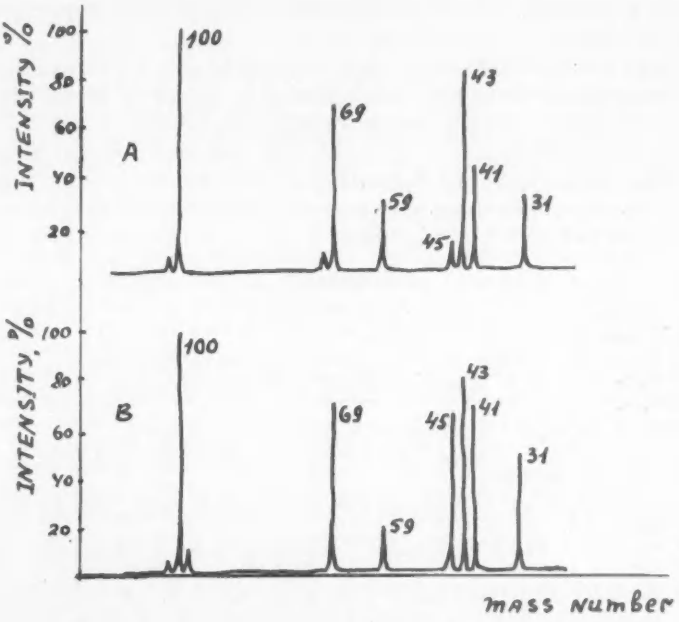

Fig. 7. Mass spectra of (*A*) methyl methacrylate; (*B*) material under investigation.

cases. Mass spectra of both substances are also practically equal. It should be noticed that in spectra of product obtained bands corresponding to masses bigger than 100 (molecular weight of monomer) are absolutely absent.

All these phenomena permit the supposition that degradation of polymers in the glasslike state at low temperature have some peculiarities which differentiate them from the usual mechanical destruction process which proceeds without formation of considerable quantities of low molecular weight products. The natural conclusion is that the chain reactions of depolymerization play a major role under these conditions. Without this supposition it is difficult to explain the appearance of considerable quantities of monomer and oligomers in the degraded system. We believe that exact explanation and understanding of the phenomena observed which are not yet clear and need further investigation must include peculiarities regarding phase state of the polymer–monomer system. One of these is that process of mechanical degradation proceeds at temperatures below melting points of monomer consisting the units of polymer chain. We can not now come to a definite conclusion about the reasons and exact mechanism of this unusual degradation process, but it may be that the peculiarities of equilibrium in the crystalline monomer–glasslike polymer system influence the character of the overall process and give the considerable quantities of monomer. The chemical structure of polymers subjected to degra-

dation, particularly their tendency in general to the chain depolymerization, for instance, on heating, must also be considered.

At any rate the realization of chain processes of polymer degradation at low temperatures for a short time oblige us to suppose a mechanism for which the value of activation energy for degradation is small.

Thus the application of mechanochemical methods for investigation of processes of synthesis and degradation of polymer chains permit us to discover and to observe some quite unusual reactions in solid state which are interesting for further investigation.

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Synopsis

Experimental results on polymerization of acrylamide, methacrylamide, and methyl methacrylate in crystalline state are discussed. The reaction is carried out under the conditions of intense mechanical disintegration of the monomer solids in the temperature range from −180°C. up to the melting point. The process of disintegration is carried out in the presence of inorganic solids, such as sodium chloride, barium sulfate, and quartz, which act as catalysts of monomer polymerization in the solid state. A crystalline state is shown to be necessary for such rapid mechanochemical polymerization of methacrylamide. The reaction proceeds with high rate up to −180°C., which indicates a very low value of activation energy. The ability to participate in such polymerization is related to some ordered state of monomer molecules combined with their mobility in the continuously renovated surface layer of dispersed crystals. Assumptions have been made about the elementary reactions of polymer chain formation and some results in mechanochemical copolymerization of two monomers in solid state are discussed. The polymerization at low temperatures is accompanied by mechanical degradation of polymer chains formed. If the mechanical degradation of some vinyl polymers is performed at a temperature below the melting point of the corresponding monomers this process may proceed as chain reaction with the formation of observed quantities of monomer. The continuous addition of mechanical energy to the system results in the shift of the chemical equilibrium between crystalline monomer and solid polymer and causes depolymerization. The reasons for this equilibrium shift are discussed; it is concluded that in the solid state rapid mechanochemical polymer degradation as well as fast polymerization is possible. Both types of processes must include a specific mechanism with very low value of activation energy.

Résumé

Les résultats expérimentaux concernant la polymérisation de l'acrylamide, du méthacrylamide et du méthacrylate de méthyle à l'état cristallin sont discutés. La réaction s'effectue dans des conditions de désaggrégation mécanique intense des monomères à l'état solide dans le domaine de température qui va de −180°C au point de fusion. Un tel processus de désaggrégation est effectué en présence de solides inorganiques tels le chlorure de sodium, le sulfate de baryum, le quartz etc. qui agissent comme catalyseur de polymérisation d'un monomère à l'état solide. On montre que l'état cristallin du méthacrylamide est nécessaire à ce genre de polymérisation mécanochimique rapide. La réaction se déroule à une vitesse élevée jusqu'à −180°C, ce qui met en évidence la très faible valeur de l'énergie d'activation. La possibilité d'effectuer de telles polymérisations est mise en rapport avec un état ordonné des molécules de monomères ainsi qu'avec leur mobilité sur l'étendue de la surface continuellement renouvellée de cristaux desagrégés. On émet certaines hypothèses à propos des réactions élémentaires responsables de la formation des chaînes polymériques et on discute certains résultats concernant la copolymérisation mécanochimique de deux monomères à l'état solide. Les processus de polymérisation à basse température s'accompagnent de la dégradation mécanique des chaînes polymériques qui se sont formées. On a montré que si l'on réalise la dégradation mécanique de certains polymères vinyliques à une température inférieure au point de fusion du monomère correspondant, ce processus peut se dèrouler comme une réaction en chaîne avec formation de quantités observables de monomères. L'introduction d'énergie mécanique dans le système produit un déplacement de l'équilibre chimique existant entre le monomère cristallin et le polymère à l'état solide et provoque la dépolymérisation. Les causes de ce déplacement d'équilibre sont discutées et on en conclut qu à l'état solide, aussi bien la dégradation mécanochimique rapide du polymère que la polymérisation rapide sont possibles. Ces deux types de processus impliquent des mécanismes spécifiques caractérisés par de très basses valeurs de l'énergie d'activation.

Zusammenfassung

Die bei der Untersuchung der Polymerisation von Acrylamid, Methacrylamid, und Methylmethacrylat im kristallinen Zustand erhaltenen Ergebnisse werden diskutiert Die Reaktion wurde unter intensiver mechanischer Zerkleinerung des festen Monomeren im Temperaturbereich von −180°C bis hinauf zum Schmelzpunkt durchgeführt. Der Zerkleinerungsprozess wird in Gegenwart gewisser anorganischer Feststoffe wie Natriumchlorid, Bariumsulfat, Quarz usw. ausgeführt, die als Katalysatoren für die Polymerisation des Monomeren im festen Zustand wirksam sind. Es wird gezeigt, dass für eine solche schnelle mechanochemische Polymerisation das Methacrylamid in kristallinem Zustand vorliegen muss. Die Aktivierungsenergie ist sehr niedrig, denn die Reaktion verläuft noch bei −180° mit hoher Geschwindigkeit. Die Durchführung einer solchen Polymerisation wird durch einen gewissen Ordnungszustand der Monomermoleküle in Verbindung mit ihrer Beweglichkeit in der ständig erneuerten Oberflächenschicht der dispergierten Kristalle ermöglicht. Es werden Annahmen über die Elementarreaktionen der Polymerkettenbildung gemacht und einige Ergebnisse bei der mechanochemischen Copolymerisation im festen Zustand diskutiert. Die bei niedrigen Temperaturen ablaufenden Polymerisationsprozesse werden von einem mechanischen Abbau der gebildeten Polymerketten begleitet. Der mechanische Abbau gewisser Vinylpolymerer bei Temperaturen unterhalb des Schmelzpunktes des entsprechenden Monomeren dürfte als Kettenreaktion unter Bildung der beobachteten Monomermengen vor sich gehen. Die stetige Zufuhr mechanischer Energie zum System führt zu einer Verschiebung des chemischen Gleichgewichtes zwischen kristallinem Monomerem und festen Polymeren und verursacht die Depolymerisation. Es werden die Ursachen für diese Gleichgewichtsverschiebung diskutiert und man kommt zu dem Schluss, dass im festen Zustand der rasche mechanische Polymerabbau ebenso wie die rasche Polymerisation möglich ist. Beide Prozesse müssem über specifische Mechanismen mit sehr niedriger Aktivierungsenergie verlaufen.

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Procédé Nouveau pour la Préparation des Polymères Silaniques Constitués par des Atomes de Carbone et de Silicum dans les Chaînes Principales

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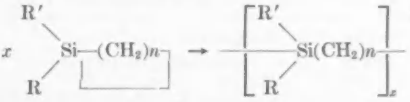
Cherchant à préparer des polymères à atomes de silicium dans les chaînes principales, nous avons étudié la polymérisation des combinaisons hétérocycliques suivant le schéma (1).



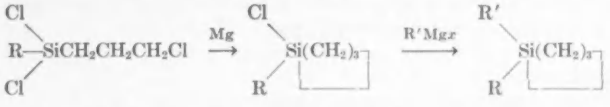
(1)

avec n = 3,4,5.

La bibliographie ne fournit que des notes de caractère préliminaire sur la polymérisation des silanes hétérocycliques.[1–3]

Nous présentons dans ce mémoire quelques renseignements sur la polymérisation des combinaisons silicacyclobutaniques. La réaction a été conduite dans des ampoules de verre scellées, sous les températures de 150 à 200°C.

Nous avons préparé les silicacyclobutanes d'après le schéma (2) suivant:



(2)

avec R = CH_3, Cl; R′ = CH_3, C_2H_5, n-C_4H_2, CH_9CH = CH_2, C_6H_5, $CH_2C_6H_5$; X = Cl, Br, I.

La méthode que nous avons mise au point nous a permis d'obtenir des silicacyclobutanes chlorés en silicium avec des rendements élevés. Dans ces dernières combinaisons la liaison Si—Cl est extrêment active. C'est la raison pour laquelle nous avons pu facilement trouver les conditions dans lesquelles le groupement silicacyclobutanique se conservait, tandis que le chlore était substitué par différents radicaux et groupements fonctionnels. Les propriétés des silicacyclobutanes sont resumées dans le Tableau I.

Sur l'exemple de la polymérisation du 1,1-diméthyl-silicacyclobutane (Tableau II) nous avons montré que la variation de la température et de la durée de la réaction ne modifie sensiblement que le rendement en polymère. Dans tous les cas il se forme des hauts-polymères solubles, dont la

TABLEAU I

Caractéristiques des Silicacyclobutanes Substitués en 1,1

No.	$RR'Si(CM_2)_3$ R	R′	Eb., °C. (mm de Hg)	n_D^{20}	d_4^{20}
1	Cl	CH_3	103,5 (755)	1,4482	0,9854
2	CH_3	CH_3	80,2–80,5 (755)	1,4250	0,7700
3	C_2H_5	CH_3	65,0–65,5 (160)	1,4392	0,7920
4	n-C_4H_9	CH_3	65,5–66,0 (25)	1,4455	0,8025
5	C_6H_5	CH_3	61,5–62,0 (5)	1,5349	0,9511
6	$CH_2C_6H_5$	CH_3	75,5–74,0 (5)	1,5313	0,9400
7	$CH_2CH=CH_2$	CH_3	53 (50)	1,4571	0,8150
8	Cl	Cl	114,5–114,8 (760)	1,4620	1,1920

TABLEAU II

Polymerisation de $(CH_3)_2Si(CH_2)_3$: Variation du Rendement et de la Viscosite Intrinsèque [η] avec le Temps et la Température[a]

No.	Durée, °C	Température de la réaction, °C	Rendement, %[b]	Viscosité intrinsèque[c] [η]
1	1	150	5,9	—
2	3	150	7,9	1,06
3	6	150	12	1,1
4	9	150	21	1,3
5	3	120	—	—
6	3	160	30	—
7	3	170	55	1,17
8	3	180	85	1,04 (1,3)[d]
9	3	200	85	1,1

[a] La polymérisation a été conduite dans des ampoules sèches traitées par la flamme nue, soufflées à l'argon sec; atmosphère d'argon.

[b] Le rendement a été déterminé après qu'on eût fait le vide dans les ampoules jusqu'à masse constante (85°/15 mm de Hg).

[c] [η] a été déterminée en solution dans le benzène à 20°C.

[d] [η] a été mesurée après reprécipitation du polymère par le methanol à partir d'une solution dans le benzène.

viscosité intrinséque varie peu suivant les conditions de polymérisation. Nous avons trouvé que la réaction étudiée sur l'exemple de 1,1-diméthylsilicacyclobutane était générale pour tous les silicacyclobutanes que nous avons étudiés (Tableau III). Dans tous les cas indépendamment du caractère des radicaux, il se forme des polysilanes hauts-polymères solubles. La composition élémentaire des polymères répond dans tous les cas à la composition des combinaisons monomères.

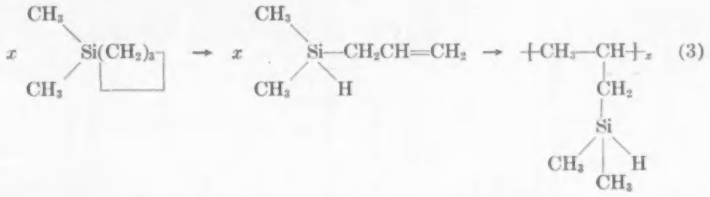
L'accroissement de la masse moléculaire du polymère obtenu à partir de l-méthyl-1-éthylsilicacyclobutane à mesure que la température de la réaction s'élève, résulte probablement du pontage du polyméthyléthyl-

silicacyclobutane comme conséquence de l'élimination du radical éthyle thermiquement instable. Un phénomène analogue a lieu probablement dans le cas de poly-1-méthyl-1-allylsilicacyclobutane.

Les polysilicacyclobutanes formés ayant des masses molécularies élevées, il est clair que pour ponter il suffit de faire réagir un très petit nombre de radicaux de ramification. Nous jugeons de la constitution des polymères obtenus d'après leurs spectres d'absorption infrarouges.

Les spectres des monomères et des polymères diffèrent sensiblement entre eux. Les spectres des polymères ne contiennent notamment pas les fréquences caractéristiques du groupement silicacyclobutane.

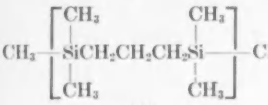
La formation de polymères contenant le silicum dans la chaîne latérale pourrait être représentée par la schèma (3):



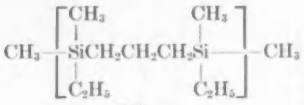
(3)

Toutefois dans les spectres de tous les polymères il manque des Canoles de fréquences caractéristiques de la liaison Si-H (plage de 2000 à 2200 cm^{-1}) et qui sont généralement très fortes.

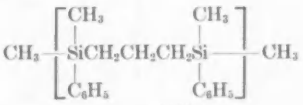
Pour la comparaison aux spectres des combinaisons polymères nous avons préparé plusieurs individus chimiques (I, II, III) qui contenaient les mêmes groupements structuraux qui avaient été présumés dans les polymères.



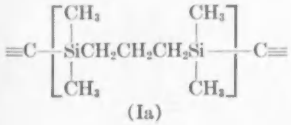
(I)



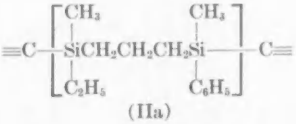
(II)



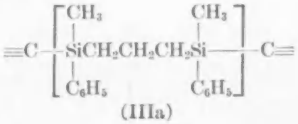
(III)



(Ia)



(IIa)



(IIIa)

TABLEAU III
Polymérisation et Propriétés des Polysilicacyclobutanes[a]

No.	R du monomère dans la formule $R(CH_3)Si(CH_2)_3$	Température de la réaction, °C	Durée de la réaction, h	Rendement, %[b]		Viscosité intrinsèque $[\eta]$[c]		Solubilité dans le benzène[d]	Aspect extérieur du polymère
				Sans reprécipitation	Après reprécipitation	Sans reprécipitation	Après reprécipitation		
1	CH_3	180	3	85	—	1,04	1,1[e]	Sol.	Bloc solide, translucide, blanc; Film: transparent, élastique.
2	CH_3	160	3	90	—	0,78	—	Sol.	"
3	C_2H_5	150	3	28	—	2,3	—	Sol.	Bloc et film blanc, analogue au caoutchouc.
4	C_2H_5	160	3	45	—	5,6	—	Sol.	"
5	C_2H_5	180	1	100	—	—	—	Insol.	Bloc gonfle facilement dans le benzène.
6	C_2H_5[f,g]	180	0.25	—	—	—	2,3	Sol.	Bloc et film incolore, analogue au caoutchouc.
7	n-C_4H_9	160	3	50	—	1,5	—	Sol.	"
8	CH_2—CH=CH_2	150	3	25	—	—	—	Sol.	"
9	CH_2—CH=CH_2	160	3	66	—	—	—	Sol.	"

10	CH_2—CH=CH_2	170	3	100	—	—	—	Insol.	Bloc gonfle facilement dans le benzène.
11	C_6H_5	160	3	—	70	—	1,1	Sol.	Bloc et film: incolore, analogue au caoutchouc.
12	C_6H_5	180	3	—	78	—	1,52[h]	Sol.	"
13	$CH_2C_6H_5$	160	3	—	—	—	1,1	Sol.	"
14	$CH_2C_6H_5$	180	3	—	53	—	1,0	Sol.	"
15	n-OC_7H_{15}	180	3	100	—	—	—	Insol.	Bloc gonfle facilement dans le benzène.

[a] La réaction a éte effectuée dans des ampoules sèches rincées par le mélange de bichromate de potassium et d'acide sulfurique dans une atmosphère d'argon.

[b] Voir le Tableau II.

[c] Voir le Tableau II.

[d] La dissolution totale dans le benzène a été constatée après 12 h de gonflement à 20° et 3 h d'ébullition, pour un rapport de 0,5 à 2,0 parties de polymère par 100 parties de solvant.

[e] Le rapport molaire monomère:solvant = 1/2.

[f] En solution dans la decaline.

[g] Masse moléculaire (déterminée par la diffusion de la lumière) = 0.8×10^6.

[h] Masse moléculaire (déterminée par diffusion de la lumière) = 5×10^6.

Les unités structurales (Ia, IIa, IIIa) sont des polymères obtenus respectivement à partir de 1,1-diméthylsilicacyclobutane, 1-méthyl-1-éthylsilicacyclobutane et de 1-méthyl-1-phénylsilicacyclobutane.

On a trouvé que les spectres des étalons préparés et des polymères correspondants étaient analogues.

On peut émettre certains jugements sur le mécanisme de la polymérisation des silicacyclobutanes en partant des données sur l'influence des additifs (Tableau IV).

TABLEAU IV

Polymerisation de $(CH_3)_2Si(CH_2)_3$: Influence du Solvant, de la Surface du Récipient Réactionnel et des Additifs sur le Rendement et la Viscosité Intrinsèque[a]

No.	Conditions de la réaction	Température, °C	Rendement, %[b]	Viscosité intrinsèque $[\eta]$[c]
1	Sans additifs	150	5.5	1,07
2	Sans additif, dans le vide (10^{-3} mm de Hg)	150	4.5	—
3	Oxygène	150	18	0,64
4	Eau	150	17	1,06
5	Verre en poudre	150	60	2,15[d]
6	Hydroquinone (2 mol.-%)	150	78	—
7	α-Naphtol (2 mol.-%)	150	70	—
8	En solution dans l'heptane[e]	160	89	0,88
9	En solution dans la tetraline[e]	160	88	—
10	Diphénylamine (2 mol.-%)	160	0	—
11	Hydroquinone (4 mol.-%)	160	91	1,58
12	Triéthylamine (2 mol.-%)	160	0	—

[a] La polymérisation a été conduite dans des ampoules sèches traitées par la flamme nue, soufflées a l'argon sec, atmosphère d'argon; durée de la réaction: 3h.

[b] Cf. Voir le Tableau II.

[c] Voir le Tableau II.

[d] $[\eta]$ a été mesurée apres reprécipitation du polymère par le methanol à partir d'une solution dans le benzène.

[e] Au cours de la polymérisation avec solvant on maintenait le rapport moléculaire monomère/solvant = 1/2.

Les données du Tableau IV permettent d'écarter probablement le mécanisme radicalaire de la polymérisation des silicacyclobutanes que l'on attribue généralement aux réactions purement thermiques.

En partant des données expérimentales que nous avons obtenues, nous avons tiré les conclusions suivantes.

1. L'accroissement de la surface des parois de l'ampoule augmente d'un ordre décimal le rendement en polymères. Dans le cas des processus radicalaires thermiques il faut par contre s'attendre à un ralentissement brutal de la vitesse de la réaction.

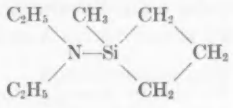
2. Les inhibiteurs classiques des réactions radicalaires comme l'hydroquinone et l'α-naphtol ne ralentissent pas le processus de polymérisa-

tion. Au contraire, en leur présence le rendement en polymère augmente sensiblement.

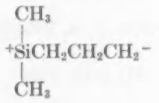
3. On sait que la diphénylamine est aussi un inhibiteur des réactions de polymérisation radicalaires. On suppose qu'en interrompant les chaînes il forme un radical stable. Cet inhibiteur s'est révélé efficace dans les cas de polymérisation considérés par nous.

Toutefois en chauffant le monomère en présence de l'inhibiteur à 150–200° dans un résonateur, on n'a pas obtenu de signaux de résonance paramagnétique électronique témoignant de la formation de radicaux. Les signaux de RPE n'ont pas été observés non plus lors de la polymérisation de 1,1-diméthylsilicacyclobutane et de 1-méthyl-1-phénylsilicacyclobutane menée jusqu'a l'obtention d'un rendement quantitatif de polymères. (Il faut dire que l'absence de signaux de RPR a pu résulter encore d'une trop faible concentration de radicaux, ce qu'indique notamment la masse moléculaire élevée des polymères.)

4. La polymérisation est aussi activement inhibée par la triéthylamine qui n'agit pas en tant qu'inhibiteur de la polymérisation radicalaire. Ainsi que nous l'avons établi le 1-(diéthylamine)-1-méthyl-silicabutane



ne se polymérise pas du tout. Toutes ces données sur l'inhibition de la polymérisation par les amines des différentes classes pourraient s'expliquer, si l'on se représentait la polymérisation des silicacyclobutanes comme intervenant par le stade de l'ouverture hétérolytique du cycle:



Dans ce cas, grâce à la présence dans l'atome de l'azote d'un couple d'électrons libre, on peut aisement se représenter l'interaction des amines avec l'extrémité électropositive de la particule. On a émis l'opinion[4] que les réactions qui interviennent par l'intermédiaire de l'ion siliconium R_3SI^+ doivent être inhibées par des amines.

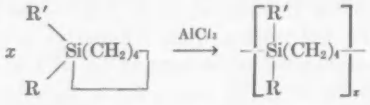
A présent nous étudions en détail le mécanisme de la polymérisation thermique des silicacyclobutanes et la possibilité de sa réalisation avec des catalyseurs et des initiateurs.

Outre la polymérisation thermique des silicacyclobutanes nous avons étudié aussi la possibilité de polymériser le 1,1-diméthylsilicacyclobutane ainsi que des silicacyclopentanes et des silicacyclohexanes thermiquement stables en présence d'halogénures de métaux en quantités catalytiques.

Les halogénures de cette série ($AlCl_3$, $AlBr_2$, $TiCl_4$, $SnCl_4$ etc.) que nous avons étudiés présentent, comme on le sait, les propriétés des acides de

Lewis, capables de provoquer le réarrangement des liaisons Si-C dans les organo-(chloro)-silanes.[4]

Pourtant, dans les conditions de la réaction que nous avons choisies: température de 0–100°C, pression normale, teneur en catalyseur 1–6% molaires, seuls les halogénures d'aluminum se sont révélés comme des catalyseurs efficaces, leur influence se bornant d'alleurs aux silicacyclopentanes. Suivant les conditions de la réaction nous avons obtenu soit des polymères huileux, à masse moléculaire modérée (de $1 \cdot 10^3$ à $3 \cdot 10^3$), soit des polymères insolubles, analogues au caoutchouc. Nous avons établi que la réaction de polymérisation des silicacyclopentanes (4)



(4)

dépend du caractère des radicaux.

Elle ne se déroule que dans le cas où les radicaux R et R′ sont des alcoyles ou l'hydrogène, dans les cas où R et R′ sont le chlore ou des radicaux aryles la polymérisation n'a pas lieu.

Nous avons également étudie (en collaboration avec le professeur L. S. Polak) la polymérisation des silicacyclanes à quatre ou à cinq membres sous l'effet des rayonnements.

Nous avons notamment établi que sous l'action du rayonnement γ ces corps peuvent se polymériser à des températures inférieures à 70°C.

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2. Vdovine, V. M., K. S. Puchtchevaya, et A. D. Pétrov, *Dokl. Akad. Nauk SSSR*, **141**, 843 (1961).
3. Vdovin, V. M., K. S. Puchtchevaya, N. A. Bélikova et al., *Dokl. Akad. Nauk SSSR*, **136**, 96 (1961).
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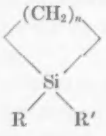
Résumé

Beaucoup de travaux ont été consacrés à la polymérisation des composés organosiliciques non-saturés. Dans le cas de la polymérisation des dérivés monoalcénoylés du silicium il se forme des macromolécules contenant des atomes de silicium dans la chaîne latérale. Pour préparer des polymères organosiliciques avec des atomes de silicium dans la chaîne principale nous avons étudié les réactions d'ouverture des hétérocycles du type

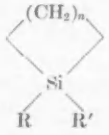


n étant égal à 3, 4, 5, sous l'action des températures élevées et de catalyseurs électrophiles. Nous avons montré qu'il était possible de preparer des hauts-polymères siliciés à atome de silicium dans la chaîne principale en polymérisant les silicacyclobutanes substitués en 1,1 ($n = 3$). Nous avons étudié l'influence de divers radicaux au niveau de l'atome de

silicium ainsi que des conditions de la réaction sur la profondeur de polymérisation et le rendement en polymère. Nous avons étudié la constitution et certaines propriétés des polymères obtenus.

Synopsis

The polymerization of unsaturated organosilicium compounds has been studied by several authors. In the case of the polymerization of mono-alkenyl-silicium derivatives macromolecules are formed containing silicon atoms in the side chain. In order to prepare organosilicium polymers with silicon atoms in the main chain ring opening reactions of the following type have been considered:



where n is equal to 3, 4, 5. The reactions were carried out at high temperatures, with electrophilic, nucleophilic, and radical mechanisms. It was possible to prepare silicon high-polymers with silicon atoms in the main chain by polymerization of 1.1 substituted silica-cyclobutanes ($n = 3$). The influence of the various radicals on the silicon atoms has been considered, as well as the influence of the reaction conditions on the extent of polymerization and the yield in polymer. The constitution and some properties of the polymer have been examined.

Zusammenfassung

Viele Arbeiten wurden schon der Polymerisation ungesättigter Organosiliziumverbindungen gewidmet. Im Falle der Polymerisation von Monoalkenylderivaten des Siliziums bilden sich Makromoleküle mit Siliziumatomen in der Seitenkette. Zur Darstellung von Organosiliziumpolymeren mit Siliziumatomen in der Hauptkette wurden Ringöffnungsreaktionen an Heterozyklen vom Typ A

n gleich 3,4,5 unter Einwirklung höherer Temperaturen und elektrophiler, nukleophiler, und radikalischer Katalysatoren untersucht. Es war möglich Hochpolymere mit Siliziumatomen in der Hauptkette durch Polymerisation von 1,1-substituierten Silicocyclobutanen (Typ A, $n = 3$) darzustellen. Der Einfluss verschiedener Radikale am Siliziumatom sowie der Reaktionsbedingungen auf die Polymerisation und den Umsatz wurde untersucht und ebenso die Konstitution und gewisse Eigenschaften der erhaltenen Polymeren.

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Un Catalyseur Efficace pour la Polymérisation des Composés Vinylsiliciques

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On sait que la polymérisation des composés monovinyl-alcoyl-(phényl)-siliciques en présence d'initiateurs peroxydés (même sous des pressions jusqu'à 6000 atm), ainsi qu'en présence de catalyseurs ioniques ne conduit pas à la formation de produits à masse moléculaire élevée.[1,2] En utilisant le système catalytique de Ziegler on a obtenu à partir du triméthylvinyl-silane des produits à masses moléculaires élevées, le taux de conversion étant toutefois réduit, de 2 à 3%.[3,4] On trouve dans la bibliographie une description de l'addition des combinaisons organolithiennes à la liaison double des molécules fortement conjuguées, notamment au 1,1-diphényl-éthylène, aux fulvènes etc., ainsi qu'aux diènes conjuguées lorsque la polymérisation est amorcée par des initiateurs. Plusieurs chercheurs[5] sont d'avis que les composés vinylsiliciques présentent un décalage de la densité électronique, probablement dû à la participation des électrons π de la liaison multiple dans la saturation des orbitales vacantes de l'atome de silicium. Cela se manifeste par le fait que les composés vinylsiliciques se comportent dans un certain nombre de réactions comme des systémes conjugués. C'est ainsi que les alcoyl-(phenyl)-vinylsilanes additionnent les combinaisons organolithiennes de manière que la partie anionique du groupement attaquant vienne s'additionner sur l'atome de carbone β du groupement vinylique.[6,7] Les sels aromatiques de diazonium s'additionnent sur les vinylsilanes dans des conditions normales avec des rendements élevés suivant la réaction de Meerwein.[8] Cette réaction est caractéristique des oléfines conjuguées, et l'on ne connaît que quelques cas où elle se déroule avec des liaisons doubles isolées les conditions étant toutefois dures.[9]

Ainsi, dans un certain nombre de réactions d'addition les combinaisons vinylsiliciques se comportent comme des systèmes conjugués. D'autre part il est bien connu que les combinaisons organolithiennes sont des catalyseurs actifs dans la polymérisation des oléfines conjuguées.

Partant de là nous avons utilisé pour la première fois les combinaisons organolithiennes pour la polymérisation des combinaisons monovinyl-siliciques et nous avons montré qu'il était possible de préparer des polymères organosiliciques à partir des monomères indiqués avec des rendements élevés.

On a étudié la polymérisation catalytique des alcoyl-(phenyl)-vinylsilanes de formule générale $R_3SiCH{=}CH_2$, R étant CH_3; C_2H_5; C_4Hg et C_6H_5 en présence de lithium éthyle ou butyle dans *n*-heptane.

Les triméthyl-, triéthyl-, et tributylsilanes ont été préparés à partir de vinyltrichlorosilane et des réactifs de Grignard respectifs alors que les diméthylphényl- et les méthyl-diphénylvinylsilanes étaient obtenus à partir de vinyltrichlorosilane et de méthyl,-phenylhalogénures de magnésium par substitution échelonnée. Les monomères obtenus ont été soigneusement séchés et rectifiés.

Quelques propriétés des combinaisons monovinylsiliciques sont indiquées dans le Tableau I.

TABLEAU I

Combinaison vinyl-silicique	Eb., °C/mm de Hg	d_4^{20}	n_D^{20}	MR_D Trouvé	MR_D Calculé
$(CH_3)_3SiCH{=}CH_2$	54–55/760	0.6938	1.3902	34.24	34.44
$(CH_3)_2C_6H_5SiCH{=}CH_2$	69/9	0.8886	1.5061	54.27	54.26
$(CH_3)(C_6H_5)_2SiCH{=}CH_2$	136–137/2	0.9974	1.5712	73.94	74.08
$(C_2H_5)_3SiCH{=}CH_2$	144–145/740	0.7722	1.4344	48.04	47.97
$(n\text{-}C_4H_9)_3SiCH{=}CH_2$	122–123/13	0.7981	1.4496	76.20	75.87

Les essais de polymérisation ont été effectués dans un réacteur de verre en atmosphère d'argon, sous des températures de −60 à +75°C pendant une durée de quelques minutes à 8 heures, la concentration de lithium éthyle variant de 2 à 20% (réduite au monomère). Les monomères solides ont été précipités, rincés et desséchés dans le vide à 50–60°C.

Les conditions et les résultats des essais de polymérisation de triméthylvinylsilane sont indiqués dans le Tableau II. Ainsi que le montre ce tableau le rendement maximum en polymères solides est observé à la température de 25°C.

Les polyvinyltriméthylsilanes obtenus dans ces conditions sont des produits pulvérulents de coloration blanche. Le polyvinyltriméthylsilane à

TABLEAU II

Polymérisation de Triméthylvinylsilane en Présence de Lithium Éthyle[a]

Solvant (heptane), ml	Température, °C	Rendement en polymères solides, %
4	−60	—
13	0	—
4	25	95
14	28	90
4	50	71

[a] Charge en monomère: 5.0 g (0,05 mole); charge en catalyseur: 4×10^{-3} mole (8% du monomère); durée: 8 h.

masse moléculaire d'environ 20,000 a une température de ramollissement voisine de 260°C. et se dissout dans le toluène. A 0°C. et aux températures plus basses on n'observait pas la formation de polymères solides à partir de styrène dans le monomére, on assistait à la polymérisation de triméthyltrimethylvinylsilane. Toutefois à 0°C, en présence de traces de vinylsilane avec un rendement de 20% en polymère solide (durée de polymérisation 8 heures). Cela s'explique probablement par le fait qu'en présence de traces de styrène l'amorçage de la polymérisation du dit monomère est considérablement facilitée. Dans le spectre d'absorption infra-rouge du polymère de polyvinyltriméthylsilane les vibrations symétriques de déformation du groupe CH_3 donnent une bande d'absorption intense à 1247 cm^{-1}. Quant à l'ensemble des bandes à 1247, 818 et 676 cm^{-1}, il est caractéristique du groupement structural $Si(CH_3)_3$. La diffraction des rayons X du polyvinyltriméthylsilane présente un anneau net de d = 5,7–5,9 Å.

Outre l'anneau le diagramme présente un fond dû aux gaz. Cela témoigne, probablement, de la présence de zones à arrangement du type gaz-cristal dans l'édifice des macromolécules.

Le Tableau III indique les conditions et les résultats d'expériences relatives à la polymérisation de diméthylphénylvinylsilane. Il convient de noter qu'à la concentration de lithium éthyle égale à 8% on n'observait pas de variations sensibles de rendements en polymères solides dans l'intervalle de températures étudiées, entre 0 et 75°C pendant 8 heures. A 50°C et aux concentrations de lithium éthyle comprises entre 2 et 20%, les rendements en polyvinyldimethylphénylsilanes solides s'élèvent à 75-95% pour des durées s'échelonnant de quelques minutes à 8 heures. Dans tous les cas, les polyvinyldiméthylphénylsilanes étaient des produits pulvérulents de coloration blanche, à temperatures de ramollissement de

TABLEAU III

Polymérisation de Diméthylphénylvinylsilane en Présence de lithium éthyle[a]

Charge en catalyseur		Solvant (heptane), ml	Température, °C	Durée, h	Rendement en polymères, %
mole $\times 10^{-3}$	% du monomère				
4	8	14	−65	8	—
4	8	4	0	8	80
4	8	4	25	8	90
1	2	4	50	0.05	76
1	2	8	50	1	78
3.5	7	7	50	8	95
6	12	22	50	8	95
7	14	14	50	8	95
10	20	23	50	8	90
4	8	8	75	8	95

[a] Charge en monomère: 8,1 g (0,05 mole).

TABLEAU IV

Polymérisation de Triéthylvinylsilane, Tri-*n*-butylvinylsilane et Méthyldiphénylvinylsilane en Présence de Lithium éthyle

Monomère			Catalyseur		Solvant (heptane), ml	Température, °C	Durée, h	Rendement en polymères solide, %
Formule	g	mole	mole × 3	% du monomère				
$(C_2H_5)_3SiCH{=}CH_2$	7.1	0.05	4	8	4	25	8	93
$(C_2H_5)_3SiCH{=}CH_2$	7.1	0.05	4	8	4	50	8	71
$(n\text{-}C_4H_9)_3SiCH{=}CH_2$	11.3	0.05	4	8	10	50	8	92
$(n\text{-}C_4H_9)_3SiCH{=}CH_2$	11.3	0.05	4[a]	8	10	50	8	93
$CH_2(C_6H_5)_2SiCH{=}CH_2$	11.2	0.05	4	8	10	75	2	80

[a] Lithium butyle.

120–130°C, solubles dans le benzène, le toluène et autres solvants organiques. Le polymère de diméthyl phénylvinylsilane obtenu avec le lithium éthyle à la concentration de 2% (50°C, 1 heure) avait une masse moléculaire d'environ 20,000. Par polymérisation de méthyldiphénylvinylsilane on a également obtenu le polyvinylméthyldiphénylsilane—un corps pulvérulent decoloration blanche à température de ramollissement d'environ 200°C (Tableau IV). Dans la diffraction des rayons X par le polyvinyldiméthylphénylsilane et le polyvinylméthyldiphénylsilane le fond dû aux gaz constitue la partie principale de l'intensité de diffusion. La présence du fond dû aux gaz montre que la structure de ces polymères est dans une large mesure non-homogène. Les variations de la température de polymérisation n'influent pas sur la structure des polymères.

Dans les spectres d'absorption infra-rouges de diméthylphénylvinylsilane et de méthyldiphénylvinyl silane on observe les fréquences caractéristiques d'absorption des groupements CH_3 ainsi que du noyau benzénique monosubstitué. Nous avons étudié également la polymérisation de triéthylvinylsilane et de tributylvinylsilane. Les résultats des expériences sont résumés dans le Tableau IV. Par leur aspect extérieur le polyvinyltriéthylsilane et le polyvinyl tributylsilane sont analogues aux polymères précédemment obtenus à partir des vinylsilanes. Les deux polymères sont solubles dans les solvants organiques. Le polyvinyltriéthylsilane dont la masse moléculaire était voisine de 60,000 présentait une température de ramollissement de 230°C. La masse moléculaire de polyvinyltributylsilane était de 40,000. L'analyse radiocristallographique a montré que le polyvinyltributylsilane était un corps amorphe, tandis que le polyvinyltriéthylsilane est caractérisé par son état intermédiaire entre le polyvinyltriéthylsilane et le polyvinyltributylsilane. Dans les spectres d'absorption infra-rouges des polymères de triéthylvinylsilane et de tributylvinylsilane on aperçoit nettement des bandes intenses qui correspondent aux fréquences d'absorption caractéristiques des radicaux éthyle et butyle de l'atome de silicium.

La teneur en silicium de tous les polymères étudiés des vinylsilanes correspondait à la teneur en silicium des monomères de depart. Dans les spectres d'absorption infrarouges de tous les polymères on constate une bande d'absorption à 1332–1337 cm^{-1} qui peut être attribuée aux vibrations de déformation dans le groupement $-\underset{|}{CH}-$. Les bandes d'absorption, correspondant à des vibratins de divers types du groupement vinylique au droit de l'atome de silicium n'ont pas été décelées.

Ainsi la présence de fréquences caractéristiques de groupements dans les spectres des polymères de monovinylsilanes permet de confirmer a structure suivante:

$$-CH_2-\underset{\displaystyle R_1-\underset{\displaystyle R_3}{\underset{|}{Si}}-R_2}{\underset{|}{CH}}-$$

On a effectué aussi la synthèse de tetraméthylphénylvinyldisiloxane et l'on a étudié la possibilité de polymériser cette combinaison en présence de lithium éthyle dans l'heptane normal aux basses températures de 0° à −60°C. On sait qu'au-dessus de 0°C les disiloxanes réagissent avec les lithium alcoyles avec formation de silanolate de lithium et de silanes tetra-substitués.[10] Toutefois dans les conditions de nos expériences nous n'avons pas réussi à obtenir des quantités notables de polymère solide, probablement à cause des réactions indiquées.

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Résumé

On sait que, parmi les composés organosiliciques non-saturés les dérivés vinyliques siliciés sont fabriqués dans nombre de pays à l'échelle industrielle. Toutefois, jusqu'à ces temps derniers, la polymérisation des dérivés monovinylalcoylés (phénylés) du silicium, conduite aussi bien en présence d'initiateurs peroxydés (même sous des pressions jusqu'à 6000 atm), qu'en présence de catalyseurs ioniques, ne menait pas à la formation de hauts-polymères. L'utilisation du catalyseur de Ziegler a bien permis d'obtenir des produits macromoléculaires à partir de triméthylvinylsilane, mais le taux de conversion ne dépassait pas 2 à 3%. Nous avons utilisé pour la première fois des combinaisons organolithiques en vue de polymériser les dérivés monovinyliques du silicium et nous avons montré qu'il était possible d'obtenir des polymères organo-siliciques à partir des monomères mentionnés avec des rendements atteignant 90%. Nous avons étudié la polymérisation catalytique des dérivés monovinyliques du silicium, de formule générale: $R_3SiCH{=}CH_2$, R étant CH_3, C_2H_5, C_4Hg, et C_6H_5 en présence de lithium-alcoyles. La polymérisation se déroulait entre −60° et +75° sous des concentrations de lithium-alcoyle entre 2 et 20%. Nous avons étudié l'influence de la structure des monomères, de la température et de la durée de polymérisation, ainsi que de la teneur pour-cent du catalyseur, sur le rendement et les propriétés des polymères obtenus. Les polymères préparés se présentaient sous forme de corps pulvérulents à températures de ramollissement élevées. Nous avons étudié la constitution ainsi que certaines propriétés des polymères obtenus.

Synopsis

Among unsaturated organosilicum compounds, vinylsilicum derivatives are prepared in several countries on an industrial scale. However, up to the last years, the polymerization of monovinyl-alkyl(phenyl)silicum derivatives, carried out either in the presence

of peroxidic initiators, (at 6000 atm.), either with ionic catalysts, was unable to form high polymers. The use of Ziegler catalyst gives macromolecular compounds from trimethyl-vinyl-silanes, but the degree of conversion never exceeds 2 to 3%. We have used for the first time organolithium compounds for the polymerization of monovinyl silicium derivatives, with a yield of about 90%. We have studied the catalytic polymerization of monovinyl silicium derivatives of formula $R_3SiCH{=}CH_2$ where R was CH_3, C_2H_5, C_4Hg, and C_6H_5, in the presence of lithium-alkyl. The polymerization proceeds between $-60°$ and $+75°C$ at concentration of alkyl lithium between 2 and 20%. We have examined the influence of the structure of the monomer, the influence of the temperature and of the duration of polymerization, the influence of the per cent of catalyst on the yield and properties of the polymer. The polymers are solid powders with a high glass transition point; their constitution and some properties have been examined.

Zusammenfassung

Es ist bekannt, dass unter den ungesättigten Organosiliziumverbindungen in einer Anzahl von Ländern die Silizium-Vinylderivate in industriellem Massstab erzeugt werden. Bis zuletzt aber hat die sowohl in Gegenwart peroxydischer Starter (selbst unter Drucken bis zu 6000 Atm) als auch in Gegenwart ionischer Katalysatoren durchgeführte Polymerisation von Monovinylalkyl-(Phenyl)-derivaten des Siliziums nicht zur Bildung von Hochpolymeren geführt. Die Verwendung eines Ziegler-Katalysators erlaubte die Gewinnung makromolekularer Produkte aus Trimethylvinylsilan, der Umsatz stieg aber nicht über 2 bis 3%. Hier wurden zum ersten Male Organolithiumverbindungen zur Polymerisation der Monovinylderivate von Silizium verwendet und es war möglich aus den angegebenen Monomeren Organosiliziumpolymere in Ausbeuten von bis zu 90% zu erhalten. Die katalytische Polymerisation von Monovinylderivaten des Siliziums der allgemeinen Formel: $R_3SiCH{=}CH_2$ wo R CH_3, C_2H_5, C_4Hg, oder C_6H_5 ist, in Gegenwart von Lithiumalkylen. Die Polymerisation erfolgte zwischen $-60°$ und $+75°$ bei Lithiumalkyl-Konzentrationen zwischen 2 und 20%. Es wurde der Einfluss der Struktur der Monomeren, der Polymerisationstemperatur und -dauer sowie des Prozentgehaltes an Katalysator auf die Ausbeute und die Eigenschaften der erhaltenen Polymeren untersucht. Die dargestellten Polymeren fielen in Gestalt pulverförmiger Substanzen mit hoher Erweichungstemperatur an. Die Konstitution und gewisse Eigenschaften der erhaltenen Polymeren wurden untersucht.

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Suppression du Stade d'Initiation dans une Polycondensation du Second Type: Ouverture des β-Lactones par les Bétaïnes

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La polymérisation de la β-propiolactone:

$$n \begin{matrix} CH_2—CO \\ | \quad | \\ CH_2—O \end{matrix} \rightarrow [—CH_2—CH_2—CO—O—]_n$$

qui n'avait pas permis d'obtenir de polyesters à masse moléculaire élevée jusqu'à ces dernières années[1–4] a fait l'objet de nombreux travaux en 1962. Les résultats antérieurs sont consignés sur le Tableau I.

Ce tableau rassemble toutes les polymérisations ou télomérisations de la β-propiolactone non substituée, signalées dans la littérature,[4–34] sauf: l'apparition accessoire de polymères lors de la réaction de la propiolactone avec divers sels d'acides minéraux,[25–27] le chlore,[8] le bioxyde d'azote,[28] les chlorures et anhydrides d'acides,[29,30] les alcools ou les phénols[31]—éventuellement en présence d'acide ou de base—les organo-magnésiens;[18] les copolymères de la propiolactone avec l'éthylène,[32,33] le butadiène,[34] les monomères vinyliques[35–37] le trioxanne,[38] le tétrahydrofuranne[39] ou le métaphosphate d'éthyle;[40] les travaux concernant la polymérisation de la propiolactone induite par les rayonnements,[9,37,41–45] qui s'effectue uniquement sur le monomère à l'état solide, et dont le mécanisme ionique n'est pas universellement reconnu; les copolymères alternés éthylène–anhydride carbonique[46] ayant une structure identique à celle des polymères de la propiolactone.

Lorsque plusieurs concentrations en un même catalyseur ont été essayées par un même auteur, seule a été indiquée celle conduisant au meilleur rendement en polymère, ou à la masse moléculaire la plus élevée. Nous avons dû exclure également de ce tableau des polymères de viscosité intrinsèque ou réduite inférieure à 0,2 ou obtenus avec un rendement trop faible,[16] ou encore insuffisamment caractérisés.[6,7,18,19,47]

Cherdron, Ohse, et Korte[5] ont récemment discuté le mécanisme de cette polymérisation, amorcée par les agents anioniques ou cationiques, caractérisée par l'existence d'une réaction d'initiation A distincte de la réaction de propagation B.

TABLEAU I

Polymérisation et Télomérisation de la β-Propiolactone (BPL) (Littérature)

Initiateur		Conditions de polymérisation				Polymère obtenu			
Nature	Concentration, mol/100 mol BPL	Temps, h	Température, °C	Solvant vol/mol BPL	Autres facteurs et remarques	Masse moléculaire moyenne	Viscosité relative correspondante	Rendement, %	Référence
Chaleur seule		100	100	Pas		(faible)		10	5
		2 et 5	130–150	Pas		(faible)		∼100	6,7
		6	135–145	Pas		∼1000		∼100	8
Pyridine									4,9,10
Potasse	0,8	336	10–15	Toluène	4 vol de solvant		1,38	62	11
	1,3	23	50	Toluène	"		0,42	90	11
	0,8	144	10–15	Pas	"		0,39	97	11
Acétate de potassium			50				0,1	70–80	11
Acétate de sodium	100	1	20	Eau		276	"	50	12,13
	20	4	15	Eau		276	"	67	12,13
	10	4	15	Eau		492	F = 30–40°C	86	12
Dichlorure d'éthyl aluminium	1	21	50	Pas			1,01	17,5	14
	1	21	50	Pas	+1/6 mol d'eau		1,8	32	14
Chlorure de diéthyl aluminium	1	21	50	Pas			1,85	12,8	14
	1	21	50	Pas	+1/3 mol d'eau		4,04	85	
Ethylate de diéthyl aluminium	1	21	50	Pas			1,72	16,6	14
Triéthyl aluminium	1	21	50	Pas			4,37	8,5	14
				Pas	+2/3 mol d'eau		9,5	18	14
									15
Butyl lithium	1	72	−78	Toluène	5 vol de solvant			64,9	16
Naphtalène sodium	1,14	18	20	Ether		Insoluble dans $CHCl_3$		10	4,16
		1	101	Dioxanne				50	

	1	101	Dioxanne					50	
Lithium + benzophénone	1	72	−78	Toluène	5 vol de solvant		<0,2	12	16
Caprate de sodium	20		30–85	Eau		388	[a]	75	13
Phtalate disodique	10		<45	Eau		540	[a]		13
Carbonate de potassium		240	10–15		2,3 vol de solvant[a]		0,35	44	11
Acide sulfurique	0,37		60–80			870		82	6,7,17
Perchlorate d'acétyle	0,1	96	20				2,5	55	5
Chlorure ferrique	0,18		25	Pas	(explosif)				6,7
	4,4		80	Benzène					6,7
Chlorure d'aluminium	0,1	21	50	Pas	Traces d'eau		0,7	22	5,6,14
Isopropylate		20	−20 à 0				0,5	82	15
d'aluminium	1	20	0					62,2	16
Potassium + benzophénone	1	26	15	Pas			<0,2	50,6	17
Iodure d'éthyl magnésium	1	72	−78	Toluène	5 vol de solvant		<0,2	39,4	17,18
Diéthyl zinc	1	25	15		2 mol-% O_2 par rapport à $ZnEt_2$		0,15	39,5	15,17
Diéthyl cadmium	1	25	15	Pas	0,1–2 mol-% O_2 par rapport à $CdEt_2$		≯0,2	5,6–22,3	17
Phosphite d'éthyle	200	6	Ordinaire	Pas	CH_3ONa 2,3 mol	1147 (sol) 460 (liq)			19
	25	~20	25	Pas	$(C_2H_5)_3N$ 5 mol	490 (liq)		~100	20

[a] Après acidification.

[b] La soude est moins active que la potasse.[11]

[c] Voir aussi les références 21–24. L'efficacité des carbonates alcalins se classe dans l'ordre K ≃ Rb > Cs > Na.[11]

I. POLYMERISATION DES β-LACTONES PAR LES AMINES TERTIAIRES

A. Cas Général

Si on utilise par exemple comme initiateur une amine tertiaire, il se forme vraisemblablement dans le stade A une bétaïne,[10,48,54] selon la réaction:

$$NR_3 + \begin{array}{l}CH_2\text{—}CH_2\\ |\quad\quad |\\ O\text{—}\quad CO\end{array} \rightarrow R_3N^{\oplus}CH_2CH_2COO^{\ominus} \qquad (A)$$

qui permet alors au stade de propagation B de se manifester:

$$R_3N^{\oplus}CH_2CH_2COO^{\ominus} + \begin{array}{l}CH_2\text{—}CH_2\\ |\quad\quad |\\ O\text{—}\quad CO\end{array} \rightarrow R_3N^{\oplus}CH_2CH_2COOCH_2CH_2COO^{\ominus} \qquad (B_1)$$

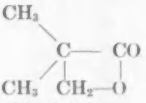
$$R_3N^{\oplus}[CH_2CH_2COO]_2^{\ominus} + \begin{array}{l}CH_2\text{—}CH_2\\ |\quad\quad |\\ O\text{—}\quad CO\end{array} \rightarrow R_3N^{\oplus}[CH_2CH_2COO]_3^{\ominus} \qquad (B_2)$$

Les réactions B_1, B_2, etc....qu'on peut considérer comme identiques entre elles, sont nettement différentes de la réaction d'initiation A qui, seule, entraîne une formation de liaisons carbone-azote et provoque l'apparition de charges importantes sur des molécules qui, primitivement, n'en comportaient pas. Si les cinétiques k_B des réactions B_1, B_2, ..., B_n, sont vraisemblablement comparables, ou égales entre elles, il n'y a par contre aucune raison pour qu'elles soient identiques à celle k_A de la réaction A d'initiation.

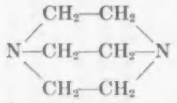
B. Cas de β-Lactones Monomères α,α-Disubstituées

Dans le cas de β-lactones monomères α,α-disubstituées, l'atome de carbone β est rendu électrophile par la présence des substituants sur l'atome de carbone α, ce qui facilite son attaque, par l'anion $—COO^{\ominus}$. La réaction B est rapide devant la réaction A. C'est pourquoi il est si difficile d'isoler la bétaïne représentant le premier terme de la réaction. Par conséquent, il n'existe dans le milieu à un instant donné qu'un très petit nombre de molécules de bétaïne susceptibles d'amorcer la naissance d'une chaîne. Celles-ci croissant jusqu'à épuisement du monomère, on conçoit qu'à partir d'une masse donnée de β-lactone substituée, il se forme alors un petit nombre de macromolécules, dont la masse moléculaire est par conséquent élevée.

C'est ainsi que la pivalolactone, ou β-lactone de l'acide diméthyl-2,2 hydracrylique, conduit facilement à des polyesters de masse moléculaire élevée en présence d'amines tertiaires, notamment celles qui, comme la triéthylène diamine, présentent un atome d'azote facilement accessible.[55,56]



Pivalolactone



Triéthylènediamine

Fischer[57] a montré que, dans ce cas, le mécanisme était apparemment conforme à celui décrit par Bauer et Magat[58] sous la dénomination de polycondensation du second type. La limite du degré de polymérisation—pour une conversion voisine de 100%—est inversement proportionnelle à la concentration en catalyseur alors qu'elle en serait indépendante dans une polymérisation anionique selon Pepper; elle ne dépend pas de la température, mais le temps nécessaire pour l'atteindre en dépend. En déterminant en fonction du temps d'une part la consommation de monomère, par pesée du polymère formé dans un milieu non solvant, et d'autre part la consommation de catalyseur, par acidimétrie de précision en milieu non aqueux, cet auteur a pu déterminer les constantes d'amorçage et de propagation.

C. Cas de β-Lactones Monomères α,α,β-Trisubstituées

Dans le cas de β-lactones monomères α,α,β-trisubstituées, la réaction A gênée par l'encombrement sur l'atome de carbone β n'a pratiquement pas lieu. Par exemple, dans les conditions habituelles, il n'est pas possible de préparer à partir de la β-lactone de l'acide 3-hydroxy-2,2-diméthylbutyrique et de triméthylamine ou même de triéthylènediamine, ni une bétaïne, ni un polymère.* Par contre, la polymerisation est déclanchée par addition d'une bétaïne préfabriquée.

D. Cas de la β-Propiolactone non Substituée

Au contraire, la β-propiolactone non substituée, dont le cycle n'est pas stabilisé par la présence de substituants, s'ouvre sous l'action des bases tertiaires selon la réaction A. Compte tenu de la faible concentration en amine tertiaire dans le milieu, cette réaction est lente, d'autant plus que le solvant constitué par l'excès de monomère lui-même est peu polaire.[50] La réaction de propagation B est également lente; le nombre de centres actifs augmentant peu à peu au fur et à mesure de la réaction, on obtiendra, à partir d'une masse donnée de monomère, de nombreuses macromolécules de masses moléculaires dispersées et relativement faibles.

Ce phénomène se trouve du reste exalté dans la pratique du fait que pour accélérer la réaction B, on est conduit à utiliser des doses relativement élevées de catalyseur NR_3 ou à chauffer. Ceci entraîne une auto-accélération de la polymérisation, qui devient violemment exothermique. Les produits de dégradation du monomère restant ou du polymère déjà formé, portés à leur température de décomposition, peuvent participer au blocage des chaînes en croissance et à la limitation de leur longueur.

II. POLYMERISATION DES β-LACTONES PAR LES BETAINES

Considérons à présent ce qui se passe lorsqu'on initie la polymérisation par une bétaïne.[59] La réaction A d'amorçage est supprimée. Si la bétaïne

* Il semble bien du reste qu'avec les catalyseurs ioniques habituels, on ne soit jamais parvenu à polymériser les β-lactones α,α,β-trisubstituées ou $\alpha,\alpha,\beta,\beta$-tétrasubstituées, du moins en produits de masse moléculaire élevée.[56,60,61]

était totalement et immédiatement soluble dans le monomère, on pourrait admettre que les chaînes se mettent à croître simultanément sur chaque centre actif, ce qui conduirait à une répartition homogène. La possibilité d'utiliser de très petites quantités de catalyseur permettrait en outre d'obtenir, à partir d'une masse donnée de monomère, un petit nombre de macromolécules à degré de polymérisation élevé.

En fait, il n'est pas nécessaire d'utiliser comme catalyseur la bétaïne provenant théoriquement de l'addition de la lactone monomère sur une amine tertiaire. Des composés de structure analogue et plus facilement accessibles, notamment la bétaïne ordinaire, ou sel interne de l'hydroxyde de (carboxyméthyl) triméthylammonium, peuvent également convenir. Toutefois, aucune des bétaïnes du type:

$$R_3N^{\oplus}(CH_2)_nCOO^{\ominus}$$

ne présente dans la β-propiolactone monomère une solubilité suffisante ou suffisamment rapide pour permettre dans la pratique l'obtention de polymères monodispersés.

D'une façon générale, l'utilisation d'une molécule fortement polarisée

$$^{\oplus}A\sim\sim\sim\sim B^{\ominus}$$

pour initier les polymérisations ioniques semble préférable à l'utilisation d'un sel:

$$A^{\oplus}\,B^{\ominus}$$

dans lequel l'un des ions seulement est utilisé pour le déclanchement, l'autre pouvant soit provoquer des réactions parasites, soit gêner pas sa concurrence de recombinaison. En faisant croître l'encombrement (et par conséquent décroître la réactivité) de l'ion non utilisé en même temps que celui de la moitié initiatrice, on supprime en quelque sorte la possibilité d'une terminaison, et on passe du mécanisme polymérisation ionique à la polycondensation du second type.

La suppression du stade d'initiation peut être étendue à la polymérisation d'autres monomères hétérocycliques, par exemple en substituant les cholines aux amines tertiaires pour la polymérisation des époxydes. Des carbanions ou des carbocations autostabilisés par une répartition adéquate des charges sur leur propre molécule constitueraient vraisemblablement des catalyseurs intéressants pour la polymérisation ionique des monomères vinyliques.

PARTIE EXPERIMENTALE

Purification des Monomères

La β-propiolactone commerciale (B. F. Goodrich Company) a été purifiée par agitation avec des granulés de chaux vive, filtration et redistillation sous pression réduite d'azote. Le lavage par une solution de soude préconisée par J. Jansen,[1] qui provoque des pertes non négligeables, a été occasionnellement effectué.

Les β-lactones des acides hydroxy-3-diméthyl-2,2-butyrique ($E^{10,5}$ = 58°C; F = 16°C) et hydroxy-3-diméthyl-2,2-valérique ($E_{4,4}$ = 58°C; F = 25°C) nous ont été confiées par le Dr. R. H. Hasek (Tennessee Eastman Company, Kingsport) qui les a préparées par addition du diméthylcétène respectivement sur l'acétaldéhyde et le propionaldéhyde.

La pivalolactone a été préparée par cyclisation de bromopivalate de sodium selon Hagman.[55,57]

Préparation des Catalyseurs

La bétaïne ordinaire (triméthylbétaïne de la glycine, ou sel interne de l'hydroxyde de carboxyméthyltriméthylammonium, Fluka Inc.) et la trigonelline (sel interne de l'hydroxyde de carboxy-3 méthyl-1 pyridinium, F. Hoffmann-La Roche) commerciales, ont été utilisées sans purification, aprés séjour en dessicateur sous pression réduite.

Deux méthodes ont été employées pour l'obtention d'autres bétaïnes: (*1*) addition du chloracétate d'éthyle ou d'un ester ω-bromé sur une amine tertiaire dans le toluène, séparation du sel précipité et traitement de sa solution aqueuse par une résine échangeuse d'ions basique (Dowex 3) (Ce dernier procédé ne convient pas pour l'obtention de la bétaïne ordinaire, le chlorhydrate d'éthoxycarbonylméthyl triméthylammonium étant décomposé avec libération de triméthylamine lors du passage sur la résine); (*2*) Addition d'une β-lactone sur une amine tertiaire. La réaction est facile avec la β-propiolactone[10,48–54] à condition d'utiliser un solvant suffisamment polaire: l'addition sur la benzyldiméthylamine n'a pas lieu dans le toluène. L'obtention de bétaïnes est beaucoup plus délicate avec la β-pivalolactone; nous n'avons pas pu la réaliser avec la γ-butyrolactone.

Polymérisation

La plupart des essais ont été effectués dans des tubes de verre sur 5 ou 10 ml de monomère, à température ordinaire. Les tubes ont été agités sur une machine à secousses ou à retournement jusqu'à dissolution du catalyseur; l'agitation a été interrompue lorsque le mélange est apparu homogène. Dans ces conditions, les bétaïnes les plus efficaces (bétaïne ordinaire, trigonelline, triméthyl bétaïnes des acides ω-aminés avec 2 ou 10 groupes méthylènes) employées à dose supérieure à 0,5% en poids, provoquent au bout de quelques minutes une polymérisation explosive bien que la dissolution apparente du catalyseur solide n'ait été que très partielle.

Pour éviter les causes d'erreur dues à une éventuelle hétérogénéité des produits de la polymérisation, ceux-ci ont été dissous dans le chlorure de méthylène tiède et coulés sur plaque métallique en films minces qui ont été soigneusement séchés. C'est sur chacun de ces films qu'ont été prélevés les échantillons pour la mesure de la viscosité intrinsèque dans le chlorure de méthylène à 25°C.

L'étude physico-chimique[62] des polyesters dérivés de la β-propiolactone et leurs possibilités d'applications[59,63] seront décrites ultérieurement.

RESULTATS

1. β-Propiolactone

a. Influence de la nature du catalyseur. Les resultats sont présentés dans le Tableau II.

TABLEAU II
Polymérisation en Masse de la β-Propiolactone à 15–20°C en Présence de 0,1 mole-% de Catalyseur azoté

Catalyseur[a]	Remarques	Viscosité intrinsèque
Pas (témoin)	Apparition de flocons après deux mois	
Triéthylènediamine	Apparition de flocons après deux mois	
Isopropylamine	Tube éclaté après un mois	0,38
Acide N-tert. butyl, amino-11-undécanoïque	Polymérisation totale en quatre mois	0,44
Acide amino-11-undécanoïque	Tube éclaté après trois mois	0,64
Acide N-isopropyl amino-11-undécanoïque	Tube éclaté après 15 jours	1,47
Benzyldiméthylbétaïne de la glycine Triméthylbétaïne de la glycine	Tube éclaté après 8 jours	1,5

[a] Le temps de dissolution du catalyseur est de quelques heures, sauf pour l'isopropylamine (immédiat).

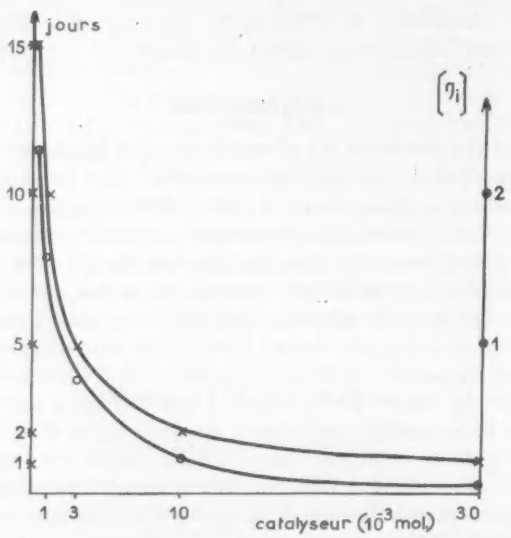


Fig. 1. Influence de la quantité de bétaïne sur la durée de la polymérisation en masse de la β-propiolactone à 15–20°C et sur la viscosité intrinsèque du polymère obtenu.

b. Influence de la Proportion de Catalyseur. La durée de polymérisation a été évaluée comme le temps au bout duquel tout liquide a disparu. Le produit est alors immédiatement dissous dans du chlorure de méthylène;

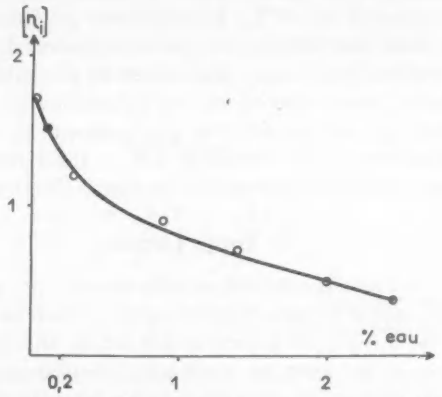


Fig. 2. Influence de la teneur en eau sur la polymérisation en masse de la β-propiolactone à 15–20°C (% d'eau en poids de monomère).

on en coule un film qui est utilisé, après séchage, pour mesure de la viscosité intrinsèque. La Figure 1 présente les résultats.

c. Influence de la Présence d'Eau. La Figure 2 montre l'influence de la teneur en eau sur la polymérisation.

TABLEAU III

Polymérisation de la β-Propiolactone par 0,2% en Poids de Benzyldiméthylbétaïne de la Glycine, dans Deux Volumes de Diluant, 10 Jours à 20°C.

Diluant	$[\eta]$	Notes
Chloroforme	0,31	
Dioxanne	0,31	[a]
Nitrométhane	0,3	[a]
Butanol	0,33	
Tétrachlorure de carbone	0,45	[b]
Ether isopropylique	0,45	[b]
Nitrobenzène	0,48	[a]
Hexane	0,5	[c]
Ether	0,6	[b]
Chlorobenzène	0,63	
Acétate d'éthyle	0,64	
Cyclohexane	0,68	[c]
Toluène	0,69	[b]
Méthyl éthyl cétone	0,74	[b]

[a] L'ensemble polymère + diluant, cireux, est précipité par un grand excès de méthanol.

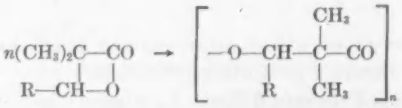
[b] Le polymère, insoluble et poudreux, est facilement récupéré par filtration.

[c] Monomère non entièrement miscible au diluant.

d. Influence du diluant. Tous les essais ont été effectués en tubes agités par retournement. On a utilisé 0,2% de benzyltriméthylbétaïne de la glycine comme catalyseur, par rapport au poids de monomère, et deux volumes de diluant pour un volume de propiolactone. Après 10 jours à température ordinaire (15–20°C), les polymères ont été filtrés ou précipités selon les cas, lavés au méthanol et mis en collodion dans le chlorure de méthylène pour coulée de film. La mesure de viscosité intrinsèque a été effectuée comme précédemment sur un échantillon de chaque film; on peut considérer que celui-ci s'écaille spontanément au séchage lorsque la viscosité intrinsèque $[\eta]$ est inférieure à 0,3; il est relativement cassant pour $0,4 < [\eta] < 0,6$ et étirable à froid au-dessus (Tableau III).

2. Autres Lactones

Les deux β-lactones α,α,β-trisubstituées ne sont pas polymérisées après plusieurs mois, soit à température ordinaire, soit au bain d'huile à 50°C, en présence de 0,1–1% de triéthylamine ou de triéthylènediamine. La polymérisation a lieu avec un rendement pratiquement quantitatif en présence d'une bétaïne, en quelques jours à température ordinaire ou en quelques heures à 80–100°C:



Si R = CH_3, le polymère obtenu après 12 heures à 100°C en présence de 0,05% en poids de triméthylbétaïne de la glycine, broyé dans un appareil Turmix, est soluble dans le chlorure de méthylène. Il fond à 185°C (sous microscope polarisant); sa viscosité intrinsèque $[\eta] = 0,74$. La polymérisation est plus longue pour R = C_2H_5, le polymère obtenu, lavé à l'acétone, fond à 150°C.

Le dimère du cétène, ou β-lactone de l'acide hydroxy-3-buten-3-oïque, traité par 0,1% de bétaïne à température ordinaire, n'a pas conduit à un polymère linéaire, mais à l'acide déhydroacétique.

La γ-butyrolactone dont le cycle n'est pas tendu, ne s'est pas polymérisée après un mois à 60°C en présence de 0,3% de triméthylbétaïne ou de benzyldiméthylbétaïne de la glycine.

CONCLUSION

Les bétaïnes polymérisent la β-propiolactone en masse à température ordinaire plus rapidement que les amines et que les meilleurs catalyseurs ioniques proposés jusqu'à présent; les rendements sont pratiquement quantitatifs et la viscosité intrinsèque des polymères obtenus est élevée. La présence d'un diluant abaisse la viscosité intrinsèque du polymère obtenu, et ceci d'autant plus que ce diluant est polaire ou susceptible de former avec le monomère un complexe polaire. Dans une polymérisation

en masse, la présence d'eau provoque un abaissement de la masse moléculaire maximale accessible.

La masse moléculaire varie en sens inverse de la proportion de catalyseur, avec laquelle augmente le temps nécessaire pour observer une conversion pratiquement complète.

L'efficacité de ce nouveau type de catalyseur est attribuée au fait qu'il permet la suppression de la réaction d'amorçage dans la polycondensation du second type.

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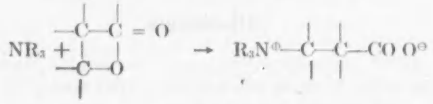
Résumé

Jusqu'à ces dernières années, les polyesters préparés à partir de la propiolactone présentaient des masses moléculaires inférieures à 1500. D'autre part, on n'était pas parvenu à polymériser certaines β-lactones substituées en β, notamment les α,α,β-trialcoyl β-propiolactones, à l'aide des catalyseurs habituels tels que les acides, bases minérales et amines tertiaires. L'utilisation de la triméthylbétaïne de la glycine et des composés de structure analogue, en quantités inférieures à 0,5%, nous a permis de préparer au

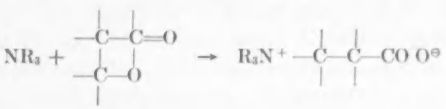
voisinage de la température ordinaire, en présence ou non de diluant, des polyesters linéaires de propiolactone non substituée dont la viscosité intrinsèque dans le chlorure de méthylène à 25° C dépasse 2. D'autre part, ces catalyseurs ont permis la polymérisation de lactones encombrées. On attribue leur efficacité au fait que la réaction d'initiation, nécessaire avec les amines tertiaires par exemple:



est supprimée lorsqu'on utilise un composé à structure bétaïnique. La cinétique globale de la polycondensation du second type ne dépend plus alors que de la vitesse de propagation. On discute l'intérêt de la suppression de cette réaction d'initiation sur la répartition homogène des masses moléculaires alternées, sur les possibilités d'atteindre des degrés de polymérisation élevés et de fabriquer des polymères séquencés.

Synopsis

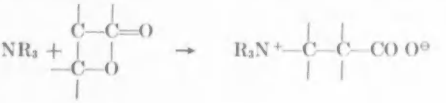
Up to the last years polyesters of propiolacton had only molecular weights lower than 1500. Moreover it was impossible to polymerize some β-substituted β-lactones, especially α,α,β-trialcoyl-β-propiolactone, with usual catalysts, as acids, inorganic bases and tertiary amines. Using glycine trimethylbetaine and analogous compounds, in amounts less than 0.5%, linear polyesters of non-substituted propiolactone can be prepared at room temperature, in the presence or not of solvent; their intrinsic viscosity in methylene chloride at 25° exceeds 2. Moreover, these catalysts make possible the polymerization of hindered lactones. It is suggested that their efficiency must be attributed to the absence of the initiation reaction, as necessary for usual tertiary amines, i.e.



The overall kinetics of polycondensation is only dependent from the rate of propagation. The influence of the absence of an initiation reaction on the homogeneous distribution of molecular weights is discussed as well as the possibility of obtaining high degrees of polymerization and of preparing block polymers.

Zusammenfassung

Bis in die letzte Zeit war es nur möglich aus Propiolacton Polyester mit Molekulargewichten unterhalb 1500 zu erhalten. Gewisse β-substituierte β-Lactone, nämlich die α,α,β-Trialkyl-β-propiolactone, konnten mit den üblichen Katalysatoren, wie Säuren, anorganischen Basen und tertiären Aminen überhaupt nicht polymerisiert werden. Die Verwendung des Trimethylbetains von Glycin und von Verbindungen mit analoger Struktur in Mengen unterhalb von 0.5% mit und ohne Verdünnungsmittel bei normaler Temperatur ermöglichte die Darstellung linearer Polyester des unsubstituierten Propiolactons mit einer Viskositätszahl in Methylenchlorid bei 25°C höher als 2. Ausserdem war mit diesen Katalysatoren die Polymerisation sterisch gehinderter Lactone möglich. Ihre Wirksamkeit wird dem Umstand zugeschrieben, dass die mit tertiären Aminen notwendige Startreaktion, z.B.:



bei Verwendung einer Verbindung mit Betainstruktur wegfällt. Die Bruttokinetik der Polykondensation zweiter Art hängt dann nur mehr von der Wachstumsgeschwindigkeit ab. Die Bedeutung einer Ausschaltung dieser Startreaktion für die homogene Molekulargewichtsverteilung und für die Möglichkeit, höhere Polymerisationsgrade zu erreichen und Blockpolymere zu erzeugen, wird diskutiert.

Discussion

H. Cherdron (*Shell Grundlagenforschung, Germany*): Avez-vous déjà essayé d'initier la polymérisation d'autres lactones comme par exemple la δ-valérolactone ou l'ε-caprolactone avec des bétaïnes préfabriquéesè

Y. Etienne: Oui. La γ-butyrolactone et la δ-valérolactone ne réagissent pas, même à chaud, ni avec les amines tertiaires, pour donner des bétaines, ni avec des bétaïnes préfabriquées pour conduire à des polymères. Par contre, le glycolide est polymérisé par les bétaïnes dès sa température de fusion.

H. Cherdron: Avez-vous dosé les groupes carboxyliques dans les polymères? Ceci permettrait de mettre en évidence la présence de quelques chaînes de faible masse moléculaire, même dans les produits de viscosité élevée.

Y. Etienne: Non.

H. Cherdron: Les rendements sont-ils à peu près quantitatifs dans tous les diluants essayés?

Y. Etienne: Les rendements sont de 99 à 100% dans les hydrocarbures, les éthers (sauf le dioxanne), es esters et le tétrachlorure de carbone. Ils sont faibles dans le butanol (36%), le nitrométhane (26%) et la méthyléthylcétone (7%). Enfin, dans le dioxanne et les hydrocarbures chlorés, ils sont compris entre 40 et 80%; dans ce dernier cas, par suite de solubilité au moins partielle, le rendement en polymère ne peut être déterminé par simple filtration et a été calculé après précipitation zu méthanol.

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Low-Temperature Solution Polycondensation

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INTRODUCTION

Many recent researches have been concerned with the mechanism and application of the interfacial polycondensation method wherein pairs of fast-reacting intermediates are combined at low temperature in two inert immiscible liquids, one of which is usually water.[1–3] Another simple polycondensation method, which is the subject of this paper,[4] comprises bringing together the same type of fast-reacting intermediates in a single inert liquid medium and providing for the removal of any acidic by-products by means of basic additives (acid acceptors). The method is designated broadly solution polycondensation, although the process encompasses both systems in which the reactants and polymer stay dissolved as well as systems in which the reactants are not all dissolved at the start and a great many from which the polymer precipitates. Solution polycondensation can be used to prepare many classes of polymers such as polyamides, polysulfonamides, polyureas, polyurethanes, and polyphenyl esters. Several types of copolymers may be prepared by proper admixing of the reactants. The low-temperature solution polycondensation process is not new, for it has been much used in the preparation of polycarbonates,[5,6] polyphenyl esters,[7] and polyurethanes from diisocyanates.[8] However, this method has not been very successfully or broadly applied previously to the more complex reaction of diacid chlorides and diamines.

RESULTS AND DISCUSSION

The following discussion is concerned with some aspects of polyamide preparation in a single liquid phase and more specifically with the reaction of terephthaloyl chloride with *trans*-2,5-dimethylpiperazine.

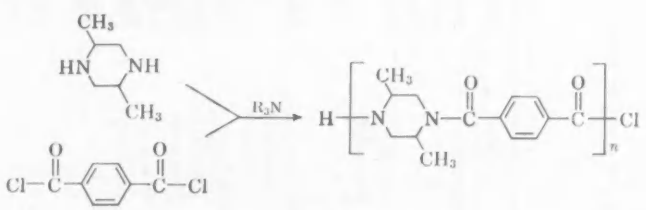

TABLE I
Properties of Some Piperazine Polymers Prepared by Solution Polycondensation

Polymerization conditions				Properties of the Product					
							Solubility[a]		
Diamine	Diacid chloride	Solvent	Method	Yield, %	η_{inh} (*m*-cresol)	PMT, °C.[b]	Formic acid	Chloroform	Dimethylformamide
Piperazine	Adipyl	Dichloromethane	A	75	0.90	350	+	−	+
	Sebacyl	Dichloromethane	A	85	1.10	200	+	+	+
	Terephthaloyl	Chloroform	C	85	1.35	>400	−	−	−
2-Methylpiperazine	Sebacyl	Dichloromethane	A	98	1.01	120	+	+	+
	Terephthaloyl	1,1,2-Trichloroethane	C	85	1.92	>375	−	−	−
cis-2,5-Dimethylpiperazine	Terephthaloyl	Chloroform	D	98	0.86	335	+	+	+
trans-2,5-Dimethylpiperazine	Oxalyl	Chloroform	C[c]	76	1.55	>400	+	−[d]	−
	Adipyl	Chloroform	A	80	1.61	290	+	−[e]	−
	Sebacyl	Hexane	C	99	1.60	165	+	+	+
	o-Phthaloyl	Chloroform	A	87	0.31	360	+	−	−[d]
	Isophthaloyl	1,2-Dichloroethane	A	90	1.44	315	+	+	−
	Terephthaloyl	*cis*-1,2-dichloroethylene	C	91	2.20	>400	+	−[e]	−
	2-Chloroterephthaloyl	Dichloromethane	A	96	0.74	>400	−	−[e]	−

cis-2,6-	Sebacyl	Dichloromethane	A	84	0.43				
Dimethyl-	Sebacyl	Dichloromethane	D	94	1.00	125	+	+	+
piperazine	Terephthaloyl	Dichloromethane	D	98	1.09	>400	−	−	−
2,2,5,5-	Sebacyl	Dichloromethane	D	90	0.76	140	+	+	+
Tetramethyl-	Sebacyl	Dichloromethane	A	99	0.89				
piperazine	Terephthaloyl	Dichloromethane	D	95	0.98	>400	−	−	−
	Terephthaloyl	Chloform	A	98	0.74				
α-2,3,5,6-	Sebacyl	Dichloromethane	D	94	0.46	120	+	+	−[d]
Tetramethyl-	Terephthaloyl	Dichloromethane	D	90	0.33	>400	+	−	−
piperazine									
β-2,3,5,6-	Sebacyl	Dichloromethane	D	80	0.46	185	+	+	−[d]
Tetramethyl-	Terephthaloyl	Dichloromethane	D	91	0.18	345	+	−	−
piperazine									

[a] The plus sign indicates solubility to at least 5% by weight at 25°C. Minus sign means insoluble at 25°C.

[b] Polymer melt temperature: lowest temperature at which a molten trail of polymer was formed when the sample was stroked with moderate pressure upon a clean metal surface.

[c] Diamine used as the acid acceptor.

[d] Partly soluble.

[e] Soluble in chloroform mixtures with formic acid or methanol.

Table I lists the results of the synthesis by the solution polycondensation ethod of some polyamides derived from piperazines.

Outline of Major Variables

Variables which affect solution polycondensations can be divided into two groups: (*1*) the properties or characteristics inherent in the pure materials and (*2*) the physical conditions selected by the operator.

Important requirements in the first class are: (*a*) a high-yield, moderately fast reaction; (*b*) an adequate solvent; (*c*) an adequate acid acceptor. Important requirements in the second class are: (*a*) purity of solvent and reactants; (*b*) equivalence of reactants; (*c*) degree of mixing and stirring; (*d*) selection and control of temperature; (*e*) time of reaction. All useful systems need not fulfill each of the requirements to an equal or an optimum degree for to some extent a lack in one respect may be overcome by high performance in another.

Reaction Rates

Solution polycondensation employs the same reactions as used in interfacial polycondensation and so similar reaction rates are involved. This means that the fastest reactions have rates of the order of 10^2–10^6 l./mole sec. Polycondensations involving such reaction rates may be completed in a few minutes at room temperature (Fig. 1). Acylations of piperazines

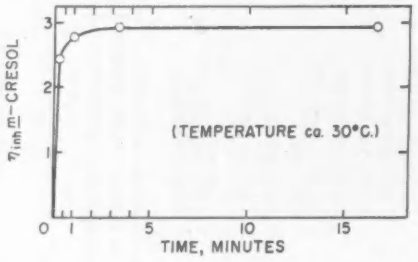

Fig. 1. Extent of polymerization vs. time for the preparation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in chloroform; Temperature about 30°C.

with not more than one methyl substituent adjacent to each nitrogen fall in this class. Although the high reaction rate provides some advantages, much slower reactions will yield polymers with high molecular weight, and fast reactions may be carried out slowly. Piperazines with two or more methyl substituents adjacent to one or both nitrogens are acylated slowly relative to the rates for the less-substituted piperazines. Thus, a wide range of acylation rates is present in this specific group of diamines.

Physical and Mechanical Effects

Temperature. Solution polycondensations between diamines and diacid halides produce polymers with the highest molecular weights when carried out at room temperature or below. Figure 2 shows a group of experiments in which both yield and the viscosity number decreased as the temperature was raised. Although reaction rates and polymer solubility would be expected to increase with temperature, there is probably a greater increase in the rate of interfering side reactions.

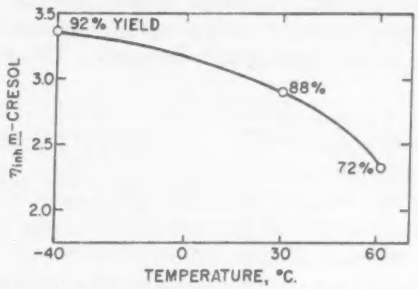

Fig. 2. Variation of extent of polymerization and yield with temperature for the preparation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in chloroform.

Concentration. Solution polycondensations have not shown any marked sensitivity to the concentration of the reactants nor to the volume ratio of the solutions except insofar as these factors may affect stirrability and temperature control. The preferred concentration range for piperazine polyamides is 1–8 g. of polymer/100 ml. of solvent.

Lower concentrations are uneconomical and introduce larger amounts of solvent impurities. Higher concentrations may yield unstirrable masses when the polymer or salt precipitates, and the heat of reaction is more difficult to control when the reactants are mixed rapidly.

Equivalence of Reactants, Mixing, and Stirring. Both interfacial polycondensations and solution polycondensations, in the faster rate range, show unusual insensitivity to nonequivalence of reactants in comparison with melt polycondensations. However, solution polycondensations are appreciably more sensitive to reactant balance than are interfacial polycondensations. For comparison, the stirred solution polycondensations of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) with rapid addition and mixing of the reactants have yielded polymers with inherent viscosities from 3 to 4, whereas interfacial polycondensation reactions with the same reagents yielded polymers with inherent viscosities from 5 to 10.

In interfacial polycondensation procedures the liquid–liquid interface performs a major role in the attainment of reactant balance. The success of the solution polycondensation reactions described here shows that the

interfacial boundary, while helpful as a regulating device, is not essential for the formation of polymers with high molecular weight. There must remain then other factors which can provide insensitivity to nonequivalence of reactants in a single-phase system.

Part of the answer is that the rate of polymerization is often faster than the rate of mixing even in the absence of an interfacial boundary. In such a solution polymerization system there are presumed to be temporary interfaces or zones within which polymerization is proceeding independently of any potential effect of the ratio of the two reactants in the system as a whole. Thus, even a single drop of acid chloride solution in a large volume of diamine solution reacts rapidly with the immediately surrounding diamine before the droplet is dispersed. This leads to oligomers

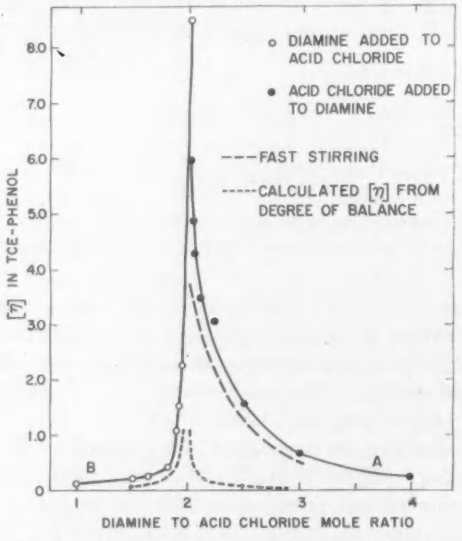

Fig. 3. Variation in extent of polymerization with reactant ratio for the preparation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in chloroform with diamine as acid acceptor.

and polymer with higher molecular weight than would be obtained from a random reaction at the known reactant ratio. Further dropwise addition of one reactant continues this effect because each successive drop goes into a large system which consists in part of active polymer with a higher than random degree of polymerization. Eventually as the system approaches equivalence and the concentration of reactive groups is reduced, there is a greater chance of wide distribution of the increment of added reactant and the occurrence of random reaction.

The data in Figure 3 show an example of insensitivity to nonequivalence of reactants which is due in part to control of the polymerization rate by

mixing and diffusion. The preparations represented by the solid lines in Figure 3 were carried out by procedure B with diamine as the acceptor. The points to the left of the peak were obtained by slow addition of diamine to acid chloride and those on the right by addition of acid chloride to diamine. The dotted lines, which are much below the solid lines for experimental results, show approximately the intrinsic viscosities which should be obtained at the various reactant ratios from a slow reaction or a reaction involving an equilibrium among the various molecular species as in the usual melt polyamidation. The system is less sensitive to excess diamine than diacid chloride, but a lower maximum molecular weight was attained by the addition of acid chloride to diamine. The difference in sensitivity is due to the behavior of diamine as an acceptor, which is explained in a later section.

Although the preparation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) is somewhat insensitive to an imbalance of reactants, it responds to careful balancing of reactants when the polymer is dissolved or highly swollen and interfering side reactions are absent. The peaks in Figure 3 were obtained by slow dropwise addition of one reactant. Since the polycondensation is not reversible and the reactants are consumed essentially as fast as added, passing beyond the equivalence point to left or right does not decrease the degree of polymerization. The major portion of the reactants can be combined rapidly with little decrease in the ultimate molecular weight.

When two solutions of reactants are combined rapidly and stirred in a blender, the degree of polymerization is more sensitive to reactant ratio, as shown by the dashed line in Figure 3. The extra-high viscosities should still be obtained from stoichiometric quantities of reactants by slow addition combined with high-speed stirring.

Acid Acceptors

A requisite for polycondensations at low temperatures of a diamine and diacid halide is that the by-product acid be removed from the reaction site, for amine salts do not react. The acceptor need not be a basic substance, but must retain the by-product acid in some way while the reaction proceeds. Tertiary amines, excess diamine, and some inorganic bases (procedure D) can be used as acceptors.

Tertiary Amine Acceptors. A wide range of tertiary amines are useful as acceptors in solution preparations of polyamides from sterically unhindered piperazines (Table II). There are base strength and solubility effects and side reactions which impose some limitations.

From an empirical point of view, the base strengths of useful acid acceptors about equal or exceed the base strength of the monoacylated diamine or, in other words, of the amine group at the end of an oligomer or polymer chain. A polymer having useful or high molecular weight is defined for the sake of discussion as one with an inherent viscosity of at least 0.6 and obtained in 75% yield. The pK_a scale in water is used for base

TABLE II
Tertiary Amine Acceptors for Preparation of Polyamides from *trans*-2,5-Dimethylpiperazine in Chloroform

Amine acceptor	pK_a in H_2O	Terephthalamide			Sebacamide		
		Polymerization mixture	η_{inh} (*m*-cresol)	Yield, %	Polymerization mixture	η_{inh} (*m*-cresol)	Yield, %
Triethylamine	10.74	Clear solution	2.97	90	Clear solution	1.60	99
Tri-*n*-propylamine	10.70	Clear solution	1.20[a]	91			
Tri-*n*-butylamine	10.89	Clear solution	1.33[a]	93			
N-Ethylpiperidine	10.45	Yellow color for short time	1.77	83			
N-Allylpiperidine	9.68	Yellow color remained	1.88	87	Clear solution	1.56	85
N-Ethylmorpholine	7.70	Cloudy at 0.5 min. but clears	2.10	87	Clear solution	1.28	90
N-Methylmorpholine	7.41	Haze at 1 min.	1.90	86	Clear solution	1.10	70
N,*N*-Diethyl-*m*-toluidine	7.24	Orange color and precipitate	1.00	90	Yellow color and precipitate	0.73	60
N,*N*-Diethyl-*p*-toluidine	7.09	Color and precipitate	1.15	85	Precipitate	0.26	70
N-Allylmorpholine	7.05	Some precipitate	1.11	86	Some precipitate	0.33	84
N,*N*-Diethylaniline	6.56	Orange color and precipitate	0.30	78			
			0.24[b]	82			
Pyridine	5.26				Precipitate at once and slight color	0.10	45

[a] Acceptor not purified.
[b] Four moles of diethylaniline (100% excess) used with each mole of diacid chloride or diamine.

strengths, although millivoltage readings in organic solvents can be used as well.

Although relative base strength is a factor in the behavior of the acceptor, it is believed that the coincidence of pK_a values of the polymer chain end and the weakest useful acceptor is fortuitous.

This relationship holds only when the polymer-forming reaction rate is high and the polymer does not precipitate rapidly. For example, the soluble poly(sebacyl piperazine) was prepared in dichloromethane in 93% yield with an inherent viscosity of 1.46 when *N*,*N*-diethyl-*m*-toluidine was the acceptor. Poly(terephthaloyl piperazine), which precipitated rapidly, was obtained in very low molecular weight. Likewise preparations with the sterically hindered diamines, *cis*-2,6-dimethylpiperazine and 2,2,5,5-tetramethylpiperazine, were unsatisfactory, although the base strengths of all the piperazines do not differ greatly.

A successful polymerization in the presence of a tertiary amine acceptor must result from the right relationship between several competing processes:

$$\text{Acid chloride} + \text{diamine} \rightarrow \text{amide hydrochloride} \quad (1)$$

$$\text{Amide hydrochloride} \rightleftharpoons \text{amide} + \text{HCl} \quad (2)$$

$$\text{Diamine} + \text{HCl} \rightleftharpoons \text{diamine monohydrochloride} \quad (3)$$

$$\text{Diamine monohydrochloride} + \text{HCl} \rightleftharpoons \text{diamine dihydrochloride} \quad (4)$$

$$\text{Acceptor} + \text{HCl} \rightleftharpoons \text{acceptor salt} \quad (5)$$

$$\text{Diamine salts} + \text{acceptor} \rightleftharpoons \text{diamine} + \text{acceptor salt} \quad (6)$$

$$\text{Acid chloride} + \text{tertiary amine} \rightleftharpoons \text{complex} \rightarrow \text{cleavage products} \quad (7)$$

Reactions (2), (3), (4), (5), and (6) and equilibria, whereas (1) and the final step of (7) are irreversible. In order for the polycondensation reaction to yield a product with high molecular weight, the second step of reaction (7) must be slow in relation to (1). If we assume for the present that the system remains homogeneous as it does for poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in chloroform, then amine ends on the polymer, diamine, and tertiary amine will all be in equilibrium with the protons at a given point. The proportion of each which is protonated presumably will be determined by their relative base strengths and concentrations. Ionization equilibria will be a secondary matter.

As acylation proceeds there will be more protons and less amine groups and free tertiary amine molecules. In spite of the apparent increasing unfavorable condition, many reactions proceed to near completion in less than a minute. For this to occur, the rate of proton transfer must be high. As the base strength of the acceptor is decreased, presumably the equilibrium becomes less favorable for maintaining the diamine and amine ends on the polymer in an unprotonated state, which is needed for acylation. A point is reached in the scale of acceptor base strengths below which only

polymers with low molecular weight are formed although the data show that this decline is not entirely abrupt.

Diamines. Piperazine and *trans*-2,5-dimethylpiperazine are unusual, though not necessarily unique, in that they can be used as both reactant and acid acceptor to produce polymers with high molecular weight by the solution polycondensation method in specific solvents. The highest molecular weight is obtained at the ratio of two moles of diamine to one of diacid chloride, regardless of the order of addition of the two solutions (Fig. 3). Polymers with low molecular weight are obtained when the polymer precipitates rapidly.

The peculiarities which make possible the use of the two piperazines as acid acceptors without interference with polymer formation are the solubilities of the diamine salts and the base-strength relationships of all of the amine species. A full accounting of the effect, even in a speculative sense, requires a consideration of various equilibria, concentration of the intermediates and products, and reaction rates. Only a brief summation is given here.

The unusual behavior of the polycondensation reaction is most apparent when diacid chloride solution is gradually added to diamine solution with stirring (right of Fig. 3). In chloroform, dichloromethane, and 1,1,2-trichloroethane, *trans*-2,5-dimethylpiperazine monohydrochloride is readily soluble, whereas the dihydrochloride is quite insoluble. During the first part of the reaction two moles of diamine act as the acceptor for each mole of acylated diamine. The diamine acting as the acceptor forms the soluble and weakly basic monohydrochloride. The large decrease in base strength (and reactivity) relative to the base strengths of the free diamine and amine groups on oligomers has the effect of removing two thirds of the diamine from full participation in the polymer forming reaction.

Precipitation of diamine dihydrochloride does not begin until a ratio of one mole of diacid chloride to three moles of diamine is reached. The polymer isolated at this point in 94% yield has a molecular weight ($\bar{M}_n$) of 6400; 98% of the chain ends bear amine groups.

As more acid chloride is added to the mixture, the average molecular weight of the polymers continues to rise, and polymerization is accompanied by a concurrent precipitation of diamine dihydrochloride. The dihydrochloride must be so insoluble and the system so sensitive to the least excess of hydrogen chloride over that required to form monohydrochloride from the nonacylated diamine that the dihydrochloride precipitates nearly quantitatively as the reaction proceeds. The results indicate a rapid transfer of protons or hydrogen chloride away from amide groups and monoacylated diamine, and the consequent existence of a high proportion of unprotonated amine ends on oligomers and the polymer chains. The participation of small equilibrium amounts of the strongly basic diamine throughout this stage of the polycondensation is postulated.

When diamine is added slowly to excess diacid chloride (left of Fig. 3), diamine dihydrochloride appears to precipitate at once. Since the ac-

ceptor action is faster than amide formation, no more than one half of the amine groups can be acylated. The polymerization must proceed locally by the mechanism just outlined. Even with the diminishing amount of amine to serve as the acid acceptor the oligomer ends are not blocked by protons for the final polymer chains end predominantly with carboxyl groups. The experimental curve for the addition of diamine to acid chloride rather than that for the opposite mode of addition, represents the effect of a high reaction rate on the relation of observed molecular weights to those calculated from the reactant ratio. Other experiments by Kwolek[9] in the absence of salt effects produce a symmetrical pair of curves and confirm this conclusion.

Solvents

Function of the Solvent. The solvent performs several functions: (*1*) dissolves the intermediates and provides for their mixing and contact; (*2*) dissolves or swells the growing polymer so that a reaction is maintained; (*3*) carries the acid acceptor and affects the removal of by-product salts; (*4*) affects the reaction rate by polarity or solvation effects; (*5*) absorbs heat of reaction.

The intermediates ordinarily are dissolved in an inert solvent before the polymerization is started. A diamine may start as an insoluble salt and be caused to dissolve because of reaction with an acid acceptor. The only conditions under which the reactants may be undissolved at the start or incompletely soluble are that solution takes place extremely rapidly or the polymer remains dissolved or swollen until all of the reactants have dissolved and been consumed.

A primary requisite for high polymer formation in all solution polycondensations is that the solvent must dissolve or swell the polymer sufficiently to permit completion of the polymerization. This point is enlarged upon in the sections on metastable polymer solutions and reactivity of precipitates. The solution polycondensation process requires a stronger polymer-solvent interaction than does the interfacial polycondensation method, yet the order of effectiveness for a series of solvents is the same. The range of solvents useful for low-temperature polycondensations is extended in the solution method to include many water-miscible solvents such as acetone, acetonitrile and dioxane. Even pyridine can be used for the preparation of poly(phenyl esters).[5–7]

For polymers prepared from diamines the adequacy of the solvent may not be determined entirely by the need for polymer solubility or swelling. The combination of solvent, diamine and acid acceptor must be such that diamine needed in the polycondensation is not precipitated as a salt with low solubility.

Metastable Solutions of Polymer. The solution polycondensation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in chloroform and certain other halogenated hydrocarbons leads to metastable or supersaturated polymer solutions. They have the normal dilute solution viscosity char-

acteristics of a polymer dissolved in a poor solvent. The intrinsic viscosity numbers are far below the values obtained by redissolving the polymer in a true solvent such as *m*-cresol (for example, 0.87 in chloroform compared to 1.35 in *m*-cresol).

The stability of these solutions varies with the solvent and increases with decreasing concentration. The solution stability in several solvents decreased in the order chloroform, dichloromethane, 1,1,2-trichloroethane, 1,2-dichloroethane. Precipitation from 1,2-dichloroethane appeared to occur at once although the precipitate was translucent and pasty. A regular array of solution stability times also resulted for polymerizations in mixtures of good and poor polymerization media (Table III). Dilute solutions in chloroform (0.1–3.6%) showed no change in viscometer flow time before visible precipitation occurred. Likewise no agglomeration of polymer molecules could be detected by light scattering before the solutions became opaque.

It has been suggested that in all solution and interfacial polycondensations a supersaturated polymer solution results, but that only in the more stable systems is observation of the effect possible. Quite stable supersaturated solutions of poly(sebacyl piperazine) have been prepared by the interfacial polymerization procedure in 1,2-dichloroethane.[3]

Selection of Polymerization Media. The point has already been made that the degree of polymerization attained in solution polycondensation is dependent to a large extent upon the solubility or swelling of the polymer by the solvent medium. Solvents can be rated directly by carrying out a polycondensation in each one and arranging the group in order of increasing or decreasing molecular weights obtained. Such a method does not take into account the possibility of interference from impurities, side reactions, or variations in starting materials. Another direct method would be to prepare the polymer by any means and measure the interactions between the polymer and solvents by the degree of liquid absorption, polymer swell-

TABLE III
Metastable Polymerization Mixtures of
Poly(terephthaloyl *trans*-2,5-dimethylpiperazine)[a]

Reaction medium, $CHCl_3$–CCl_4			Reaction medium, CHCl–hexane		
$CHCl_3$, mole-%	Time before first precipitate formed	η_{inh} (*m*-cresol)	$CHCl_3$, mole-%	Time before first precipitate formed	η_{inh} (*m*-cresol)
73.6	<5 sec.	2.79	62.6	<1 sec.	3.15
78.3	15 sec.	2.96	86.7	10 sec.	3.23
82.8	0.5–1.5 min.	3.48	93.6	1–2 hr.	3.65
84.6	5–10 min.				
89.4	2 hr.	3.70			
95.8	22 hr.	3.59			

[a] Procedure E.

ing or polymer precipitation effects. This method, which should provide valuable fundamental information, has not been studied.

An indirect method for selecting and classifying solvents for solution polycondensation employs low molecular weight compounds having structures analogous to that of the polymer. The method is applicable to limited groups of polymers but cannot be applied broadly even to polyamides without further refinements and modifications.

Briefly the method is to determine the temperatures required to form solutions of the model compounds in potential polymerization media and from these data and the melting points and heats of fusion of the models calculate excess interaction energies (K) for solution formation. In Table IV a group of solvents is arranged in order of descending values of K. It will be seen that polymerization in polar solvents has yielded higher molecular weights than predicted by K values. A plot of these and additional data as in Figure 4 with the dielectric constant as the ordinate provides a means for classifying solvents in relation to their potential use as polymerization media.

TABLE IV
Preparation of Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in Various Solvents

Polymerization medium			Results of polymerization[a]	
Solvent	K avg.,[b] cal./mole	ϵ[c]	η_{inh} (*m*-cresol)	Yield, %
Diethyl ether		4.34	0.31	45
Hexane		1.89	0.36	54
Cyclohexane		2.02	0.35	57
Carbon tetrachloride		2.24	0.38	64
Xylene	+660	2.27	0.21	67
Acetone	350	20.7	1.81	78
Methyl ethyl ketone	220	18.5	1.25	76
Acetonitrile	70	37.5	1.99	75
Dioxane	−170	2.21	1.01	85
Acetophenone	−340	17.4	1.64	85
Bromobenzene	−420	5.40	1.20	86
Nitrobenzene	−550	34.8	2.37	76
1,2-Dichloropropane	−580	8.93	1.55	74
1,4-Dichlorobutane	−680	9.06	1.08	75
1,3-Dichloropropane	−970	10.0	1.87	70
1,2-Dichloroethane	−1420	10.7	2.50	76
1,1,2-Trichloroethane	−2180	7.57	2.20	87
Dichloromethane	−2470	9.08	2.67	82
Chloroform	−3430	4.81	4.2	90

[a] Polymerization by procedure C.

[b] K avg. is the average of the excess interaction energies for the formation of solutions in the pure solvents of two diamides representing portions of the polymer structure. The diamides were 1,4-dibenzoyl-*trans*-2,5-dimethylpiperazine and terephthaloyl di(2-methylpiperidine).

[c] Dielecric constant of the pure solvent.

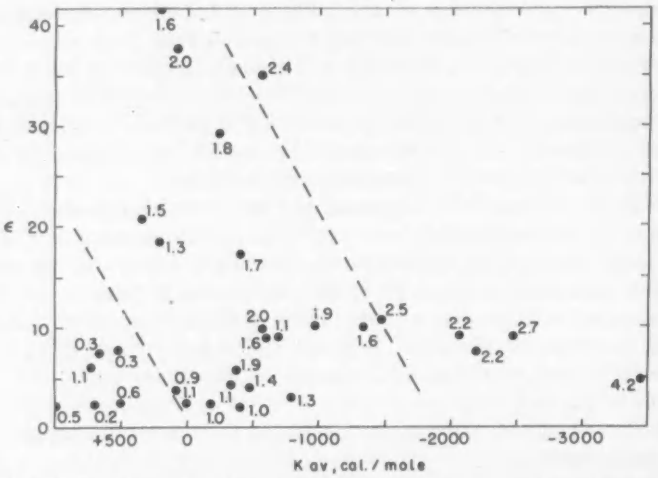

Fig. 4. Relation of the solvent dielectric constants and the average interaction energies of the solvents with a pair of model compounds to the extent of polymerization of poly(terephthaloyl *trans*-2,5-dimethylpiperazine). Numbers in the plot indicate the inherent viscosity (*m*-cresol) of the polyamide obtained by polymerization in the solvent represented by the adjacent point.

Reactivity of Polymer Precipitates

The solution polycondensation method, being free from interference by hydrolysis and control by interface effects, provides the opportunity to study any continuing reaction in the precipitated state and to determine whether the precipitates are permanently inactivated or only in a restricted state of movement and growth.

Preparations of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) were carried out in mixtures of the good solvent chloroform with two poor solvents, carbon tetrachloride and hexane (procedure C). Inherent viscosities versus solvent compositions are plotted in Figure 5. The yields were not quantitative and were somewhat variable (77–90% for η_{inh} above 0.6). In part this was due to mechanical losses.

Polymer samples prepared in poor solvent mixtures and having inherent viscosities in the range of 0.8–1.5 were isolated under anhydrous conditions in both solvent-wet and dry stages and then treated in various ways to determine whether polymerization would continue.

The experiments led to the following conclusions.

(*1*) The molecular weight of the polyamide can be controlled by use of mixtures of "poor" and "good" solvents as polymerization media, for under favorable conditions the polymer attains a molecular weight which increases with the proportion of good solvent present.

(*2*) Poor mixing and slow introduction of a reactant into a polymerization mixture from which rapid precipitation occurs leads to a molecular

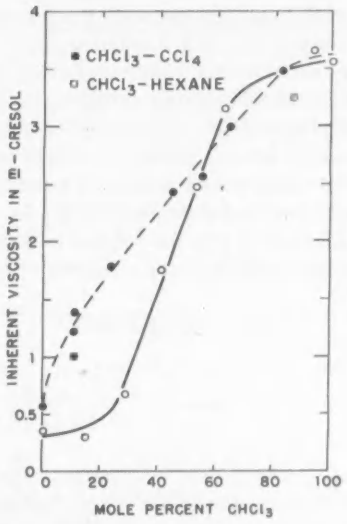

Fig. 5. Preparation of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in mixed solvents.

weight lower than that characteristic of the polymer-solvent system under optimum conditions. At least a partial recovery from this situation can be made by an extension of the reaction time.

(*3*) A polymer which has a low molecular weight because the system is lacking a portion of reactant will increase in molecular weight to that characteristic of the system upon addition of the missing intermediate and the provision of thorough stirring and an added period of time for completion of the reaction.

(*4*) The polymer precipitates are reactive and increase in molecular weight upon transfer to a stronger solvent system.

(*5*) The molecular weight of a polymer precipitate obtained in a poor solvent is increased by transfer to a highly polar solvent to a value approaching that characteristic of polymer prepared in such a solvent.

(*6*) The increase in molecular weight of polymer precipitates which occurs upon transfer to a good solvent or a polar solvent after preparation in a poor solvent results to a large extent from the interaction of complementary chain ends.

Two problems connected with the reactivity of the precipitates have not been fully resolved. The first relates to the possible precipitation of a small portion of diamine salt with the polymer from a poor solvent. The loss of diamine would contribute to the initial formation of low polymer and yet the diamine would be available for continued polymerization in good solvents containing a tertiary amine acceptor. Various washing treatments failed to demonstrate the presence of diamine salt in the polymer

precipitates. The second problem concerns the reason for continuation of polymerization upon immersion of low polymers in the polar solvents, acetone, acetonitrile and nitrobenzene (point *5* above). These solvents were rated by tests with model compounds as having lower or equal swelling power for the polymer relative to that of the initial polymerization medium. Quite possibly the model tests are incorrect. If the polar solvents are correctly rated, then they must effect continued reaction by changes in the reaction rate or effects on salt solubility and equilibria.

The preservation of reactivity in the polymer is dependent upon keeping acid chloride end groups intact and the absence of physical changes in the

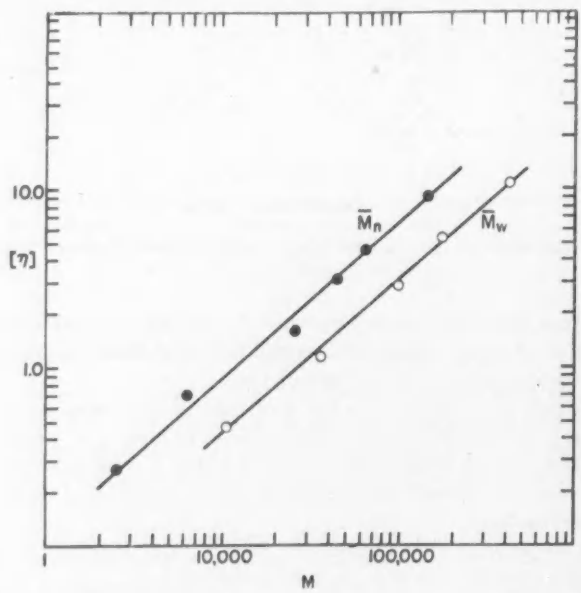

Fig. 6. Relation of intrinsic viscosity of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) in *sym*-tetrachloroethane–phenol (40:60 by wt.) to $\bar{M}_n$ from endgroup titrations and $\bar{M}_w$ by the light-scattering method.

polymer such as crystallization. Table V shows a set of experiments in which a washed precipitate was held in a wet state in a nonswelling solvent and in a dry powdered state under nitrogen. Reactivity was low in the dispersed stage after five days. The dry polymer reached a similar state in 20 days. The cause of the loss of reactivity is not known but the result could be brought about by slow hydrolysis of acid chloride groups, interaction of halogenated solvent with amine end groups, slow decomposition of an acid chloride–tertiary amine complex, or a physical change, suggested above. In all these cases, except possibly for hydrolysis, the presence of solvent would yield the observed acceleration of decay in reactivity.

Molecular Characteristics

The lower molecular weight products represented by points to the left and right of Figure 3 were composed of chains ending almost entirely in carboxyl or amine groups, respectively. Higher molecular weight polymers contained both types of end groups.

Figure 6 shows viscosity–molecular weight relationships for poly(terephthaloyl *trans*-2,5-dimethylpiperazine). Weight-average molecular weights up to 500,000 have been obtained. Since $\bar{M}_n$ and $\bar{M}_w$ values were determined on different sets of samples, no comparisons are justified.

EXPERIMENTAL

The following preparative procedures are presented as being typical of the general method whereby various types of condensation polymers can be made from fast-reacting intermediates.

A. Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) by the Solution Polycondensation Process in Chloroform with Triethylamine

Trans-2,5-dimethylpiperazine (2.28 g.) and 5.6 ml. of pure triethylamine were dissolved in 100 ml. of washed chloroform in a 500-ml. Erlenmeyer flask. To this mixture was added a solution of 4.06 g. of terephthaloyl chloride in 80 ml. of chloroform with swirling. More chloroform (20 ml.) was used to rinse in the residues of terephthaloyl chloride at once. The mixture remained clear, but the temperature rose quickly from 25 to 42°C. and there was an increase in solution viscosity. The solution could be dry-cast on glass to produce self-supporting films, which were strong and flexible if washed free of salt with water just before they were dry.

After 5 min., the product was coagulated by pouring the solution into hexane with stirring. A fibrous precipitate was obtained as well as crystals of triethylamine hydrochloride. If the precipitation was done slowly with no stirring or only slow stirring, long, coarse strings of polymer were obtained, which could be readily torn apart by hand or in a home blender. The precipitate was washed well with water and finally with acetone. After drying at 100°C. a 92% yield of polymer was obtained which had an inherent viscosity of 3.1 ($\eta_{inh} = [\ln \eta_{rel}]/c$ where c is 0.5 g./100 ml.; determined in *m*-cresol at 30°C.).

As an alternative to the above procedure with better control of reaction conditions, the polycondensation mixture was cooled with an ice bath and stirred with a magnetic stirrer. This is applicable to systems in which no heavy precipitates form.

B. Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) Prepared in Solution with Diamine as the Acid Acceptor

Terephthaloyl chloride (4.06 g., 0.02 mole) was dissolved in 150 ml. of chloroform in a 500 ml. flask equipped for fast stirring. A solution of

trans-2,5-dimethylpiperazine (4.456 g., 0.0390 mole) in 98 ml. of chloroform was added dropwise over a period of 45 min. A precipitate of diamine dihydrochloride formed as the diamine was added. A 40-ml. portion of chloroform was used to rinse the dropping funnel. A 75-ml. sample of the mixture was removed for a viscosity determination; the inherent viscosity was 1.61.

A solution of 0.20 g. of the dimethylpiperazine in 50 ml. of chloroform was then added over a period of thirty minutes. During this time the dispersion of diamine salt became very viscous. The polymer was precipitated in a fibrous form in hexane. The inherent viscosity was 5.79, and the total yield was 89%.

The experiments on molecular weight versus reactant ratio, reported in Figure 3 were carried out in this way. The initial volume of chloroform was always 150 ml. and contained either 0.02 mole of terephthaloyl chloride or 0.04 mole of 2,5-dimethylpiperazine. The volume of solution in the graduated dropping funnel was proportional to the amount of added reactant (0.20*M* in acid chloride or 0.40*M* in diamine). The temperature of the flask was kept at 25°C.

C. Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) by the Solution Polycondensation Process Under Conditions of Rapid Polymer Precipitation

For polymerizations in which polymer precipitation occurs, the quart-size home blender is a convenient device. The jar and stirrer bearing were dried and the bearing sealed and lubricated with an inert substance, such as Celvacene medium vacuum grease (Distillation Products Industries). The top was covered with aluminum foil and over this was placed the plastic cap. A wide powder funnel was inserted through a $^3/_4$-in. hole in the center of the cap and foil.

trans-2,5-Dimethylpiperazine (2.28 g.), triethylamine (5.6 ml.), and 100 ml. of benzene were placed in the blender jar. The terephthaloyl chloride (4.06 g.) in 90 ml. of benzene was added rapidly through the funnel while the stirrer was simultaneously speeded up by means of a rheostat. Traces of acid chloride were rinsed in at once with 10 ml. of benzene. A precipitate formed immediately and stirring was continued at moderate speed for 5 min. The mixture was diluted with an equal volume of hexane and the precipitate collected and washed as before. The white powder, obtained in 90% yield, had an inherent viscosity of 1.21 (*m*-cresol).

The order of mixing, that is, diamine to acid chloride or acid chloride to diamine, is not critical when mixing is fast and equivalents of reactants are used. The addition of acid chloride to diamine is preferred ordinarily because the acid chloride solution is then not exposed to humid air in the reaction vessel. Further, the system is less sensitive to excess diamine, and this order of addition provides such a situation throughout the pouring step.

D. Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) by the Solution Polycondensation Process in the Presence of an Inorganic Acceptor

trans-2,5-Dimethylpiperazine (2.28 g.) was dissolved in 100 ml. of chloroform in a blender and 5.92 g. (0.08 mole) of reagent grade, powdered calcium hydroxide was added. To this was added, over a period of 5 min. with moderate stirring, 4.06 g. of terephthaloyl chloride in 100 ml. of chloroform. Stirring was continued for 10 min. and the mixture stood 15 min. more. At no time was there any appearance of the gelatinous diamine dihydrochloride. The soluble monohydrochloride was presumed to be a likely intermediate in the reaction.

A portion of the mixture was filtered and yielded a clear solution from which very tough, transparent film was cast.

The remainder of the mixture was diluted with acetone and the precipitate was collected and washed. Washing with 2% aqueous hydrogen chloride was included to assure removal of calcium hydroxide. The over-all yield was 95% and the inherent viscosity was 3.14 (*m*-cresol).

E. Treatment of Polyamides from Solution Polycondensation to Show Increase in Molecular Weight Upon Exchange of Solvents

trans-2,5-Dimethylpiperazine (2.28 g.) and triethylamine (5.6 ml.) were dissolved in a 20:80 (by volume) mixture of washed chloroform and carbon tetrachloride in a blender. There was added quickly (5 sec.) with stirring a solution of 4.06 g. of terephthaloyl chloride in 85 ml. of the same mixture, and 15 ml. of mixed solvent was used to rinse in the last of the acid chloride. A translucent precipitate of polymer formed at once. The mixture was stirred 6 min. and a 50-ml. sample was taken.

This sample was divided and polymer isolated from half ($\eta_{inh} = 1.79$) and half held and stirred with a magnetic stirrer for 6 min. to serve as a control on the following step. The inherent viscosity of this second sample was 1.78.

The main portion of the polymerization mixture was diluted with 100 ml. of chloroform so that the chloroform–carbon tetrachloride ratio was approximately 52 to 48. This was stirred 6 min. in the blender and the polymer was isolated. The inherent viscosity of this final product was 2.72 and the total yield was 87%.

The usual method of isolation was to pour the reaction mixture into an equal volume of hexane, filter the precipitate, and wash it with water and 25% aqueous acetone. Washing with acetone may cause slight fractionation of the polymer, but washing with water alone must be thorough in order to remove all salt.

Variations of this procedure included (*1*) formation of a filter cake of polymer, washing this in a blender with nonswelling solvent, and dispersion in a swelling or polar solvent, and (*2*) isolation of a washed and dried polymer powder under anhydrous conditions followed by dispersion in a swelling solvent at various time intervals.

TABLE V
Retention of Activity in Dispersed and Dried Precipitates of Poly(terephthaloyl *trans*-2,5-dimethylpiperazine)[a]

Dispersion[b]		Dry solid[c]	
Time, hr.	η_{inh} (*m*-cresol)	Time, hr.	η_{inh} (*m*-cresol)
0	2.02	0	2.02
15	1.38	15	1.98
112	1.10	112	1.60
		280	1.29
		472	1.07

[a] Polymer prepared in 10:90 (by vol.) $CHCl_3$–CCl_4, washed twice in blender with 10:90 $CHCl_3$–CCl_4, η_{inh} = 0.84 (*m*-cresol).

[b] Held as dispersion in 10:90 $CHCl_3$–CCl_4, then stirred in $CHCl_3$ with 0.5 ml. triethylamine/100 ml.

[c] Held as dry solid under nitrogen, then stirred in $CHCl_3$ with 0.5 ml. triethylamine/100 ml.

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Synopsis

A remarkably simple process is described for the formation of high molecular weight condensation polymers from fast reacting intermediates, such as diamines and diacid halides. The method comprises reacting equivalents of the intermediates at normal temperatures in a single inert liquid and providing for the removal of byproduct acid by means of basic additives. The method is designated broadly solution polycondensation, although the process encompasses not only systems in which the reactants and polymer stay dissolved but systems in which the reactants are not dissolved at the start and a great many from which the polymer precipitates rapidly. Low-temperature solution polycondensation can be used to prepare many classes of polymers, such as polyamides, polysulfonamides, polyureas, polyurethanes, and polyphenyl esters. Copolymers and block copolymers may be prepared by proper admixing of the reactants. Solution polycondensation has been used previously, but the only reports in the literature where the achievement of truly high molecular weights has been supported by experimental data are for the preparation of polyphenyl esters (including carbonates) in pyridine solution with or without some diluent. Hydrogen transfer polymerizations, as between diisocyanates and diamines or diols, which evolve no byproducts are frequently carried out in a single solvent also. An extended study has been made of some of the polymerization variables. Among these are reactant balance, selection of solvent media, solvent polarity, basicity of the acid acceptor and reactivity of polymer precipitates.

Study of the single-phase system as opposed to the two-phase interfacial polycondensation method is leading to a better understanding of low-temperature polycondensation in general. For example, the single solvent method often has much of the insensitivity to reactant equivalence characteristic of the interfacial polycondensation process, even though, in the former system, no liquid-liquid boundaries are present. Polymer precipitates formed in an inert solvent and kept suspended or isolated as a powder retain their reactivity for many days. Under certain circumstances, the polymerization can be continued by coupling of polymer chains or by introduction of additional monomeric intermediates. Despite some limitations, the solution polycondensation process provides another route to forming new condensation polymers and to the study of the characteristics of polymers made by fast reactions under nonequilibrium conditions.

Résumé

Un processus remarquablement simple est décrit pour la formation de polymères de condensation à hauts poids moléculaires, à partir d'intermédiaires réagissant lentement, comme les diamines et les halogénures de diacides. La méthode comprend la réaction d'équivalents des intermédiaires à températures normales dans un liquide inerte unique et l'adjonction de composés basiques afin d'écarter l'acide issu d'une réaction secondaire. La méthode es appelée brièvement polycondensation en solution, bien que le procédé comprenne seulement des systèmes où les réactifs et le polymère restent en solution mais aussi des systèmes où les réactifs ne sont pas dissous au départ et dont une grande partie provoque rapidement la précipitation du polymère. On peut faire usage de la polycondensation en solution à basse température, pour la préparation de plusieurs classes de polymères, comme les polyamides, les polysulfonamides, les polyurées, les polyuréthannes et les esters polyphényliques. Les copolymères et les copolymères en bloc peuvent être préparés par addition judicieuse des réactifs. La polycondensation en solution fut employeée antérieurement, mais les seules communications de la littérature où l'obtention de très hauts poids moléculaires était étayée par des données expérimentales, concernent la préparation d'esters polyphényliques (inclusion faite des carbonates) en solution pyridinique, avec ou sans diluant. Des polymérisations par transfert d'hydrogène, comme c'est le cas pour les diisocyanates et les diamines ou les diols, qui ne donnent pas naissance à des produits secondaires, furent souvent réalisées, également dans un solvant unique. Une vaste étude de certaines variables de la polymérisation fut faits. Parmi celles-ci il y a la proportion en réactifs, le choix du milieu (solvant), la polarité du solvant, la basicité de l'accepteur d'acide et la réactivité des précipités de polymère. L'étude du système à une phase, en opposition à la méthode de polycondensation interfaciale à deux phases, mène à une meilleure compréhension de la polycondensation à basse température en général. Par exemple, la méthode du solvant unique est souvent fort indépendante de l'équivalence en réactifs, caractéristique du procédé de polycondensation interfaciale, bien que dans le premier système il n'y ait pas de plan de séparation liquide-liquide. Les précipités polymériques formés dans un solvant inerte et maintenus en suspension, ou isolés sous forme de poudre, gardent pendant plusieurs jours leur réactivité. Dans certaines conditions, la polymérisation peut être poursuivie par couplage des chaînes polymériques ou par introduction d'intermédiaires monomériques additionnels. En dépit de certaines limitations, le procédé de polycondensation en solution fournit une autre voie pour la formation de nouveaux polymères de condensation et pour l'étude des caractéristiques des polymères obtenus par des réactions lentes dans des conditions de non-équilibre.

Zusammenfassung

Ein bemerkenswert einfacher Prozess zur Bildung hochmolekularer Kondensationspolymerer aus rasch reagierenden Stoffen, wie Diaminen und Dikarbonsäurehalogeniden, wird beschrieben. Die Methode besteht in der Reaktion äquivalenter Mengen der Ausgangsstoffe bei normaler Temperatur in einer inerten Flüssigkeit und Entfernung der

als Nebenprodukt entstehenden Säure durch basische Zusätze. Die Methode wird im weiteren Sinn als Lösungspolykondensation bezeichnet, obwohl nicht nur Systeme mit reagierenden Stoffen und Polymerem in Lösung, sondern auch solche mit anfangs nicht gelösten reagierenden Stoffen und sehr viele mit rascher Ausfällung des Polymeren verwendet werden. Tieftemperatur-Lösungspolykondensation kann zur Darstellung vieler Polymerklassen, wie von Polyamiden, Polysulfonamiden, Polyharnstoffen, Polyurethanen, und Polyphenylestern herangezogen werden. Durch geeigneten Zusatz der reagierenden Stoffe können Copolymere und Blockcopolymere dargestellt werden. Lösungspolykondensation wurde schon früher verwendet, die einzigen Literaturangaben über die experimentell sichergestellte Erreichung wirklich hoher Molekulargewichte beziehen sich aber auf die Darstellung von Polyphenylestern (einschliesslich von Karbonaten) in Pyridinlösung mit oder ohne Zusatz eines Verdünnungsmittels. Auch Wasserstoffübertragungs-Polymerisationen, wie zwischen Diisocyanaten und Diaminen oder Diolen. bei denen keine Nebenprodukte entstehen, werden häufig in einem einzelnen Lösungsmittel ausgeführt. Eine ausgedehnte Untersuchung einiger Polymerisationsvariabler, nämlich des Reaktantenverhältnisses, der Auswahl der Lösungsmittel, der Lösungsmittelpolarität, der Basizität des Säureacceptors und der Reaktivität der Polymerfällungen wurde durchgeführt. Die Untersuchung des Einphasensystems im Gegensatz zur Zweiphasen-Grenzflächenpolykondensationsmethode führt zu einem besseren Verständnis der Tieftemperatur-Polykondensation im allgemeinen. Zum Beispiel besitzt die Lösungsmittel-Methode oft eine ähnliche Unempfindlichkeit gegen das stöchiometrische Verhältnis der Teaktanten wie de Grenzflächenpolykondensationsprozess, obwohl bei ersterem keine Flüssig-Flüssig-Grenzflächen anwesend sind. In einem inerten Lösungsmittel gebildete und suspendiert gehaltene oder als Pulver isolierte Polymerfällungen behalten durch viele Tage ihre Reaktivität bei. Unter gewissen Bedingungen kann die Polymerisation durch Koppelung von Polymerketten oder durch Einführung zusätzlicher monomerer Ausgangsstoffe fortgesetzt werden. Die Lösungspolykondensation bietet, ungeachtet gewisser Beschränkungen, einen weiteren Weg zur Bildung neuer Kondensationspolymerer und zur Untersuchung des charakteristischen Verhaltens von Polymeren die durch rasche Reaktionen unter Nicht-Geichgewichtsbedingungen hergestellt wurden.

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Nouvelle Classe de Cocatalyseurs dans la Polymérisation Anionique du Caprolactame

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Introduction

La polymérisation anionique de l'ε-caprolactame fut révélée il y a vingt-cinq ans environ, simultanément par Schlack en Allemagne et Joyce et Ritter[1] aux U. S. A.

Toutefois, du point de vue réactionnel, cette polymérisation ne fut étudiée que beaucoup plus tard et c'est à Hanford et Joyce[2] que l'on doit la publication des premiers travaux sur cette question.

Depuis, de nombreux chercheurs se sont penchés sur ce problème et actuellement plusieurs mécanismes de polymérisation sont proposés: citons, en particulier, les études de Wichterle et ses collaborateurs,[3] Champetier et Sekiguchi,[5] Chpitalny.[4]

Or il est connu que la polymérisation anionique du caprolactame ne se produit qu'à des températures supérieures ou au moins égales à 220°C, point de fusion du polycapramide. Au-dessous de cette température, les réactions de polymérisation n'ont pratiquement pas lieu; il faut faire alors appel à des cocatalyseurs ou "activateurs," grâce auxquels il est possible de provoquer la polymérisation à partir de 150°C.

L'action de certains activateurs du type *N*-diacylé est expliquée d'une façon satisfaisante par Wichterle, Sebenda, et Kralicek,[6] il n'en est pas de même pour d'autres composés qui peuvent également jouer le rôle d'activateurs. Ainsi, nous avons mis en évidence l'action activatrice des polyéthers et plus particulièrement du di(hydroxyéthoxy)-1,2-éthane

$$OHCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

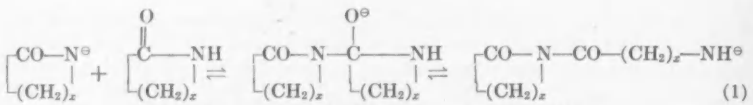
Rappel des Mécanismes Proposés

Il est admis, lors de la polymérisation des lactames, qu'au contact d'un initiateur (métaux alcalins ou organomagnésiens mixtes), il y a formation d'ions lactimate:

$$\left[\begin{array}{l} CO{-}N^{\ominus} \\ \quad | \\ (CH_2)_x \end{array}\right]$$

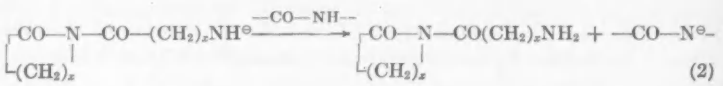
x pouvant être supérieur ou égal à 5.

La polymérisation débute par une période d'induction qui correspondrait à la formation de groupes actifs "imide," eq. (1):



(1)

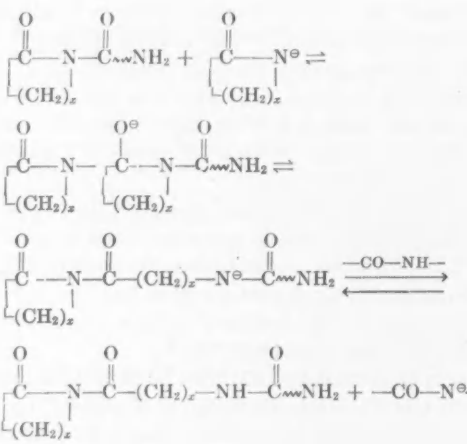
L'ion ($-NH^{\ominus}$) serait, d'après Wichterie,[3] immédiatement neutralisé en groupement amine par un groupement amide, eq. (2).



(2)

En particulier, si le groupement amide appartient à une molécule de lactame qui n'a pas réagi avec l'initiateur, il y a régénération de l'anion lactimate.

Les réactions de propagation peuvent ensuite se schématiser de la façon suivante, eq. (3):



(3)

Si les vitesses de réactions de propagation sont très grandes, en revanche, la vitesse de réaction d'induction correspondant, comme nous venons de le voir, à la formation d'un imide *N*-aminoalcoyllactame, est très faible. En particulier, dans le cas de l'ε-caprolactame, elle est pratiquement nulle en dessous de 200–220°C (P. F. du polyamide 6).

Or Sebenda et Kraličeк[6] ont montré que l'addition de *N*-alcoylimides supprimait complètement la période d'induction et, conséquence très importante, rendait possible la polymérisation en dessous de 200°C pour le caprolactame.

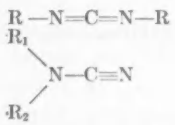
Ces imides seuls ne sont évidemment pas capables d'après les schémas réactionnels ci-dessus, d'initier la polymérisation: l'action simultanée de l'initiateur alcalin et de l'imide est essentielle pour l'obtention de polyamide par polymérisation anionique de lactame.

Diverses Classes de Cocatalyseurs

Les divers composés pouvant jouer le rôle d'activateur sont, outre les *N*-amino-alcoyllactames, la plupart des composés *N*-diacylés: citons le *N*-acétyl-caprolactame, le *N*-formylcaprolactame, la *N*,*N*,*N'*,*N'*-tétracétylhexméthylènediamine.

Bien entendu, peuvent avoir également une action cocatalytique, tous les produits susceptibles de réagir *in situ* sur le lactame pour donner des composés *N*-diacylés; c'est le cas, par exemple, des dérivés d'acide organique: halogénures, anhydrides esters, amides. Ainsi, le diméthylformamide a une action très marquée; il peut donner, en effet, le *N*-formylcaprolactame, selon la réaction:

Toutefois, l'expérience montre que d'autres corps peuvent également rendre possible la polymérisation des lactames à basse température. C'est ainsi que, outre les dérivés *N*-diacylés, la plupart des composés à azote tertiaire de formule générale A—N—B ont une action cocatalytique, A et B pouvant être des radicaux du type —C=S, —SO_2, —N=O, voire même un radical alcoyle.[7] Citons, en particulier, les composés ayant pour formule générale:



dérivés dialcoylés des formes aminonitrile ou diimine de la cyanamide.

Il nous faut également citer certains composés minéraux tel l'anhydride phosphorique; B.A.S.F.[8] revendique, en effet, toute une classe de cocatalyseurs dérivés d'acides minéraux.

Cas Particulier des Polyéthers

Pour notre part, au cours de récents travaux, nous avons pu mettre en évidence les propriétés cocatalytiques de composés possédant plusieurs fonctions éther.[9]

Parmi les composés qui ont donné des résultats positifs nous pouvons citer: des polyoxyéthylèneglycols, tels que les polyglycols 300S, 1000, 1500S, 600P de Naphtachimie et surtout le di(hydroxyéthoxy)1,2-éthane appelé communément triéthylèneglycol; des polyoxyéthylèneglycols possédant différentes fonctions terminales, tels ceux désignés commercialement par: Scurol AR et AO (de Rhône-Poulenc), condensat d'oxyde d'éthylène sur l'acide oléique, Lauropal, condensat d'oxyde d'éthylène sur l'alcool laurique, BrIJ 35 (de Atlas Powder) qui est un lauryloxyéther, Laurate de polyoxyéthylène 300 de la Société Normande de Produits Chimiques;

des polypropylèneglycols tels que le polypropylèneglycol 1025 de Union Carbide; à un degré moindre, un polytétrahydrofuranne.

D'une façon générale, ces composés ont été utilisés à la dose de 10 à 15‰ en poids de lactame.

Dans le cas particulier du triéthylèneglycol, nous avons constaté que ses dérivés mono et diméthoxylés montraient également une activité cocatalytique, sans être cependant aussi importante que celle du produit dont ils sont issus.

De plus, il est à remarquer que certains polyoxyéthylèneglycols du commerce permettant la polymérisation anionique des lactames à basse température ont leurs fonctions hydroxyle terminales bloquées par des groupements lauryloxy en particulier.

Malgré la présence, dans certains composés mentionnés ci-dessus, de groupements hydroxyle ou ester, en plus de la fonction éther, l'enchaînement R_1—O—R_2 apparait donc bien comme étant responsable de l'activité cocatalytique constatée au cours de nos essais.

Il est à signaler, cependant, que certains éthers de faible condensation en carbone, n'ont pas donné d'aussi bons résultats que les composés cités ci-dessus: ceci est probablement dû à leurs points d'ébullition qui se situent à des températures inférieures à celles de polymérisation. De même des polyoxyméthylènes industriels n'ont pu être utilisés à cause de leur insolubilité dans les lactames aux températures considérées.

Partie Expérimentale et Résultats

Les lactames utilisés au cours de nos polymérisations étaient aussi purs que possible et exempts de toute trace d'humidité.

Nous nous sommes adressés spécialement aux capro, capryl, lauryl lactames, seuls ou en mélange.

Nous avons utilisé les initiateurs classiques de polymérisation, principalement les métaux alcalins.

Le mode opératoire utilisé au labo a été le suivant. Dans un tube de verre soigneusement nettoyé et séché, on place 50 g de lactame; on ajoute 10‰ en poids de cocatalyseur parfaitement anhydre. Le tube est ensuite chauffé sous atmosphère inerte jusqu'à une température permettant la dissolution ultérieure, dans le lactame fondu, du métal alcalin. Dans le cas particulier du caprolactame, cette température est de 80°C pour le sodium et de 110°C pour le potassium. Le métal alcalin est ensuite introduit à la dose de 5‰ en poids. Le tube, soumis à un léger courant d'azote, est placé alors dans une enceinte chauffante réglée à ±1°C, à la température de polymérisation désirée et pendant une durée déterminée.

L'échantillon de polymère, ainsi formé, est ensuite retiré sans difficulté du tube de verre après refroidissement.

Les principaux résultats obtenus avec le caprolactame et le sodium comme initiateur sont mentionnés dans le Tableau I.

TABLEAU I

Polyéther, 10‰	Température de polymérisation, °C	Durée de polymérisation, h	Viscosité inhérente ds *m*-crésol
Scurol AO	180	6,67	0,75
Polypropylèneglycol 1025	"	6	0,71
Polyglycol 1300H	"	6	0,67
" 1500S	"	4	0,75
" 400S	"		
" 300H	"	4	0,75
" 600H	"	4	0,71
Laurate polyoxy 300[a]	160	4,5	1,44
Triéthylèneglycol[a]	"	3	1,04

[a] Utilisé en présence de 2,5‰ de sodium.

D'après le Tableau I, nous voyons que l'action de la fonction polyéther est plus ou moins nette selon la structure chimique du composé dont il dépend: l'effet cocatalytique est renforcé ou atténué selon la présence d'autres fonctions.

Ce point différencie assez nettement les polyéthers des autres cocatalyseurs du type *N*-diacylé par exemple. Il semble donc bien que le mécanisme de l'action de ces composés soit à considérer d'une facon différente de celle des cocatalyseurs "classiques."

Nous avons entrepris, en collaboration avec d'autres laboratories, une série d'essais en vue de préciser le mécanisme de l'action cocatalytique des polyéthers.

L'auteur tient à exprimer ses vifs remerciements à la Direction de la Société Rhodiaceta pour les encouragements dont il a bénéficié au cours de ce travail.

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Résumé

La polymérisation anionique du caprolactame débute par une période d'induction caractéristique correspondant, d'après certains auteurs, à la formation d'un imide, le *N*-aminocaproylcaprolactame; la formation de ce composé est tres lente en-dessous de

200°C et, de ce fait, l'obtention de polymère devient pratiquement impossible. Wichterle et ses collaborateurs, en particulier, ont montré que l'addition à la polymérisation de composés du même type que cet imide, c'est-à-dire de composés *N*-diacylés, accélérait beaucoup la phase d'initiation et, en particulier, la rendait possible bien en-dessous de 200°C. De tels composés sont appelés cocatalyseurs ou activateurs; vu l'intérêt pratique de cette technique de polymérisation en-dessous du point de fusion du polyamide 6, la plupart sont revendiqués dans la littérature des brevets. Or d'autres composés peuvent être employés comme cocatalyseurs; citons les urées substituées, les uréthanes, quelques anhydrides minéraux tels que l'anhydride phosphorique, etc. Si pour certains il est encore possible de concevoir des réactions d'addition avec le caprolactame, ce qui aurait pour résultat de former directement le dérivé *N*-diacylé dans le milieu réactionnel, il n'en est pas de même pour d'autres activateurs. C'est le cas, par exemple, d'une nouvelle classe de cocatalyseurs: les polyéthers. Un certain nombre, en effet, peut être utilisé en tant que tels; les meilleurs résultats semblent être obtenus avec le di(hydroxyéthoxy)-1,2-éthane, $OH(CH_2—CH_2—O)_2H$ (produit de condensation de trois molécules diéthylèneglycol). Ces produits agissent à la même dose que les composés du type *N*-diacylé; toutefois la vitesse de polymérisation est plus faible qu'avec ces derniers. Du point de vue de la température, l'action cocatalytique est observée pour le même domaine que les autres types d'activateurs, c'est-à-dire à partir de 150°C environ.

Synopsis

The anionic polymerization of caprolactam shows an initial induction period corresponding to the formation of imide, *N*-amino-caproyl-caprolactam, as assumed by some authors; the formation of this compound is very slow below 200°C., and consequently the formation of polymer becomes practically impossible. Wichterle and coworkers particularly have shown that the addition of compounds similar to this imide, i.e., *N*-diacyl-compounds, accelerated markedly the initial step, and especially make the reaction possible much below 200°. Such compounds were called "cocatalysts" or "activators"; on account of the practical interest of this polymerization technique below the melting point of nylon-6, most compounds were claimed in corresponding patents. However, other compounds can also be used as cocatalysts, i.e., substituted ureas, urethanes, some inorganic anhydrides, as phosphoric anhydride. If for some of them it is conceivable that addition reactions with caprolactam would afford directly the *N*-diacyl derivative in the reaction medium, for other activators this is not the case. For exampie with a new class of cocatalysts: the polyethers, of which some can be used directly, the best results seem to be obtained with di(hydroxy-ethoxy)1,2-ethane or $OH(CH_2—CH_2—O)_2H$ (condensation product of three molecu es of diethylene glycol). These products are active at the same doses as the *N*-diacyl compounds; however the rate of polymerization is slower. With respect to the temperature the cocatalytic action is observed over the same range of temperatures as for the other activators, i.e., from about 150°.

Zusammenfassung

Die anionische Polymerisation von Caprolactam beginnt mit einer charakteristischen, nach der Meinung mancher Autoren der Bildung eines Imides, des *N*-Amino-caproyl-caprolactams, entsprechenden Induktionsperiode; die Bildung dieser Verbindung verläuft unterhalb 200° äusserst langsam und aus diesem Grund wird es praktisch unmöglich, Polymeres zu erhalten. Im besonderen haben Wichterle und Mitarbeiter gezeigt, dass der Zusatz von Verbindungen gleichen Typs wie dieses Imid, nämlich von *N*-diacylierten Verbindungen, die Anlaufphase der Polymerisation stark beschleunigt und sie insbesonders auch unterhalb 200° möglich macht. Solche Verbindungen werden "Kokatalysatoren" oder "Aktivatoren" genannt; bedingt durch das praktische Interesse dieses Polymerisationsverfahrens unterhalb des Schmelzpunktes des Polyamids 6, wird

die Mehrzahl dieser Substanz in der Patentliteratur in Anspruch genommen. Aber auch andere Verbindungen können als Kokatalysatoren verwendet werden; es seien substituierte Harnstoffe, Urethane, einige anorganische Anhydride, wie Phosphorsäureanhydrid usw. angeführt. Für einige von ihnen ist es noch möglich Additionsreaktionen mit dem Caprolactam zu formulieren, die zur direkten Bildung des *N*-diacylierten Derivates im Reaktionsmilieu führen könnten, bei anderen Aktivatoren ist das aber nicht mehr der Fall. Das trifft z.B. für eine neue Klasse von Kokatalysatoren, die Polyäther, zu. Eine gewisse Zahl kann tatsächlich als solche verwendet werden; die besten Ergebnisse scheint Di-(hydroxyäthoxy)-1,2-äthan $HO(C_2H_2—CH_2—O)_2H$ (das Kondensationsprodukt aus drei Molekülen Äthylenglykol) zu liefern. Diese Stoffe sind in gleicher Dosis wie die Verbindungen vom *N*-Diacyl-Typus wirksam, allerdings ist die Polymerisationsgeschwindigkeit geringer als bei letzteren. Die kokatalytische Wirkung tritt im gleichen Temperaturbereich wie bei den anderen Aktivatortypen, nämlich von 150° aufwärts, auf.

Discussion

H. Sekiguchi (*Ecole de Physique et Chimie, Paris, France*): Est-ce que la période d'induction de votre polymérisation est plus longue que dans le cas de la polymérisation catalysée par les co-catalyseurs habituels, tels que les amides et les esters? Avez-vous comparé votre polymérisation, en particulier, avec la polymérisation catalysée par les esters?

Ch. Mermoud: Nous avons constaté effectivement que la période d'induction au cours des polymérisations "activées" par les polyethers était plus longue que dans le cas de la polymérisation en présence d'amide ou d'esters. Dans le cas particulier des esters, la période d'induction est legèrement plus faible que dans le cas du méthylèneglycol.

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Synthesis of New Nitrogen- and Oxygen-Containing Polymers with Conjugated Bonds from Inorganic Salts and Carbamide

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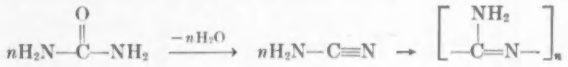
The polymers with a system of conjugated double bonds are of considerable importance as in certain cases they exhibit properties characteristic of semiconductors.

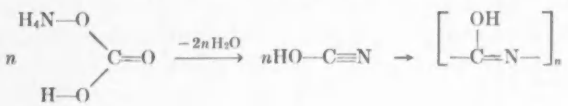
In this research we have obtained for the first time high molecular compounds consisting of the recurring structural units: polycyanamide, $-C(NH_2) = N-$, polyanic acid, and $-C(OH) = N-$.

We used urea, ammonium carbonate, and bicarbonate, and sodium carbonate, bicarbonate, and ammonium chloride as the starting materials.

The reactions proceed according to the eqs. (1)–(5):



(1)



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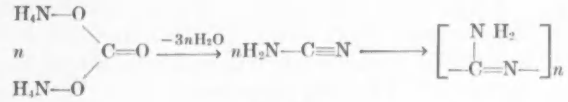

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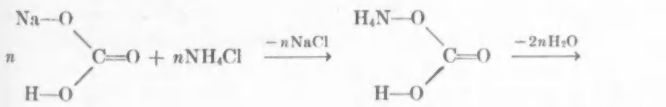

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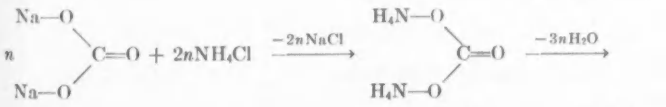

(5)

TABLE I
Influence of Experimental Conditions on the Polymer Yield

No.	Starting material	Polymer structure (repeating unit)	Conditions of experiments: Catalyst	Temperature, °C.	Time, hr.	Starting material catalyst ratio[a]	Polymer yield, wt.-% of theory
1	$H_2N-\underset{\underset{O}{\|}}{C}-NH_2$	$-\underset{\underset{NH_2}{\|}}{C}=N-$	$ZnCl_2$	300	10	1	32
2	"	"	"	"	15	"	43
3	"	"	"	"	20	"	54
4	"	"	NH_4Cl	300	1	1:2	29
5	"	"	"	"	10	"	66
6	"	"	"	"	15	"	92
7	H_4N-O $\quad\quad C=O$ H_4N-O	"	NH_4Cl	300	5	1:4	25
8	"	"	"	350	"	"	79
9	"	"	"	400	"	"	91
10	H_4N-O $\quad\quad C=O$ $\quad\quad HO$	OH $-C=N-$	NH_4Cl	300	5	1:3	28
11	"	"	"	350	"	"	82
12	"	"	"	400	"	"	96
13	$NaHCO_3 + NH_4Cl$	OH $-C=N-$	NH_4Cl	350	5	1:4	49
14	"	"	"	"	10	"	65
15	$Na_2CO_3 + 2NH_4Cl$	NH_2 $-C=N-$	NH_4Cl	350	10	1:5	61
16	"	"	"	375	"	"	73

[a] In all cases the starting material catalyst ratio is indicated as optimum.

As catalysts we used various water-absorbing compounds, such as halides (zinc chloride, ammonium chloride, etc.), phosphoric anhydride, and calcium oxide.

The experiments were carried out on solid starting materials thoroughly triturated and mixed in definite proportion (see Table I) in an autoclave free of air oxygen, under pressure and at 200–400°C. The reaction was allowed to proceed for 1–20 hours. The reaction product was washed with water to remove the catalyst and the crude unreacted materials. Then the polymer was purified with a reprecipitated acid and dried to constant weight in vacuum.

The influence of the experimental conditions on the polymer yield is indicated in Table I.

In all cases the polymers were brown powders (of either light or dark shade, depending on the duration and temperature of polycondensation), infusible, extremely thermoresistant (the loss in weight as the result of heat treatment at 1200°C. was only 5–7%), insoluble in organic solvents except dimethylformamide and easily soluble in mineral and organic acids.

The dependence of the reduced viscosity on acid concentration in the solvent displays anomalous behavior similar to that observed by Berlin;[1] this can be explained by the strong interaction of the polymer and the solvent (as a result the presence of the amino and oxy groups and the presence in the main chain of electronegative nitrogen). The value of the intrinsic viscosity is within the same range (0.05–0.15) as for the formerly described similar polymers [2]

In the infrared spectrum of the prepared polymers the band at 1600 cm.$^{-1}$ corresponds to the system of conjugated C=N double bonds, the band at 1372 cm.$^{-1}$ to the vibration of the C—NH_2— bond, the band at 873 cm.$^{-1}$ to the C—N— bond, and that at 1042 cm.$^{-1}$ to the hydroxyl group.

The prepared polymers easily form salts in acid solutions. The heats of salt formation of the polycyanamide and polycyanic acid are very similar to those of aromatic amines. The curves of potentiometric titration of the polymer acid solutions are similar in shape to those of aniline. The amine numbers agree well with the theoretical number.

The prepared polymers exhibit ESR spectra characteristic of polyconjugated systems. The number of free electrons lies in the range of 10^{17}–10^{19}.

This is the first time that new polymers with conjugated double bonds, i.e., a polycyanamide having the structure of polyaminonitrile and polycyanic acid with the structure of polyoxynitrile have been synthesized. We also worked out a new synthesis of polymers based on inorganic salts.

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[a] In all cases the starting material catalyst ratio is indicated as optimum.

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Initiation of Butadiene Popcorn Polymerization*

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Only a small amount of information has been published concerning the formation of popcorn polymer nuclei, the small nodules of insoluble polymer which possess the ability to proliferate rapidly when placed in the presence of monomer in either the liquid or vapor phase. The purpose of this paper is to discuss some of the proposed mechanisms in the light of additional experimental evidence as they apply to butadiene.

Initiation of butadiene popcorn polymerization in the laboratory has been accomplished by several techniques. The most commonly used method is to seal the monomer in a closed tube along with some water, benzoyl peroxide, and a rusty nail.[1–3] Graham and Winkler[1] found that the optimum concentration of benzoyl peroxide for popcorn initiation was 1% at 75°C. and 4% at room temperature. They observed the following order for rapidity of formation: first, the system monomer, benzoyl peroxide, water, and rusty iron; second, monomer plus benzoyl peroxide and rusty iron; third, monomer plus benzoyl peroxide.

A closed container of pure butadiene which is allowed to stand undisturbed for an extended period of time will also produce popcorn polymer.[4] In addition, Gee[5] has observed the formation of insoluble polymer during the mercury-photosensitized polymerization of butadiene.

It is universally concluded that popcorn polymerization is a free-radical mechanism and that the resultant polymer owes its insolubility to extensive crosslinking.[6,7] The first step in the formation of popcorn is undoubtedly the polymerization of the monomer in the form of a tiny, insoluble, crosslinked nucleus. Once formed, this nucleus propagates by means of numerous growing chains. These chains or network radicals have restricted mobility and since they cannot readily terminate, the resultant polymerization is very rapid.

Staudinger[8] first showed that traces of a crosslinking agent caused the formation of popcorn polymer in styrene. Whitby[4] stated that the first appearance of insoluble polymer in styrene is due to a few polymer molecules acquiring by chance a proportion of crosslinking molecules (divinylbenzene) far in excess of the average, with the result that they become highly cross-

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TABLE I
Sealed Tube Butadiene Polymer Initiation Experiments

Expt. no.	Temp., °C	Time	Tube contents: C_4H_6, g.	H_2O, g.	Bz_2O_2, mg.	Metal	Metal in phase[a]	Results	Popcorn formation
342	60	61 days	5.04	1.0	10.6	Pure Fe wire	L	Small amount of popcorn on wire, in both L and V, C_4H_6 layer very viscous	+
	RT	10 yr.							
358	60	117 days	6.49	1.0	10.8	Oxidized Fe wire	L	Small amount of popcorn on wire in L, C_4H_6 layer still fluid	+
	RT	10 yr.							
354	60	117 days	5.61	1.0	10.2	Pure Fe wire	V	C_4H_6 layer not fluid, popcorn at H_2O–C_4H_6 interface, no popcorn on wire	+
	RT	10 yr.							
350	60	61 days	5.0	1.0	11.9	Oxidized Fe wire	V	C_4H_6 layer not fluid, popcorn at H_2O–C_4H_6 interface, popcorn on glass wool plug and bottom of wire touching the glass wool	+
	RT	10 yr.							
346	60	61 days	5.69	1.0	0	Pure Fe wire	L	C_4H_6 layer still fluid, H_2O layer contains white polymer	0
	RT	10 yr.							
360	60	117 days	5.93	1.0	0	Oxidized Fe wire	L	"	0
	RT	10 yr.						"	
339	60	60 days	5.85	1.0	0	Rusty nail	L	"	0
	RT	10 yr.						"	
340	60	68 days	7.45	1.0	0	Rusty nail	V	"	0
	RT	10 yr.						"	
367	60	114 days	5.33	1.0	0	Black Fe annealed	V	"	0
	RT	10 yr.						"	
404	60	14 days	4.87	5.0	0	0	—	"	0
	RT	10 yr.						"	
466	RT	10 yr.	38.4	0	0	0	—	Complete formation of popcorn	+
2852	60	13 days	10.0	0	0	Co metal degassed	V	Formation of popcorn in 6 days	++
2864	60	48 days	10.0	0	0	Co metal	V	"	+

[a] L denotes liquid, V denotes vapor.

linked and separate, thus leading to the presence of visible specks of insoluble polymer.

Breitenbach and Fally[9] postulated that for the formation of a nucleus it was sufficient if long linear chains formed entanglements leading to microgel particles in which radicals formed by transfer had a lower probability of termination than the radicals in the mobile phase. Fox and co-workers[10] state that a small number of crosslinks must be present to produce a satisfactory nucleus, and they propose reactions which involve chain transfer with polymer chains.

EXPERIMENTAL METHOD

The experimental technique used in this laboratory for the preparation of butadiene popcorn polymer seed has been discussed in a previous communication.[11] Matheson extra-pure grade butadiene was admitted to the prepared 18 mm. Pyrex tubes by means of vacuum distillation. The tubes were pumped at −78°C. for a period of 10 min. to insure removal of air and then sealed under vacuum. The polymerizations were performed in the darkness of an oil bath at 60°C. for the indicated period. Following this many were stored in the dark at room temperature and were removed for examination on several occasions during a period of approximately 10 years. The observations recorded are those at the end of the 60°C. interval; the subsequent lengthy time period produced no change in the appearance of the products. Duplicate experiments and others containing minor variations in the amounts of components were opened at various intervals for evaluation of the contents. Only single representative experiments are included in Table I for clarity.

The cobalt metal was Baker Chemical Co., 99.5% pure. For experiment 2852 the metal was filed clean, washed, and treated *in vacuo* for 3 hr. at 400°C. prior to use. For experiment 2864 the heat treatment was omitted.

Infrared spectra of the insoluble polymers were obtained by the potassium bromide pellet technique previously described.[12]

EXPERIMENTAL RESULTS

The reported experiments (Table I) employing butadiene in the presence of a water phase were conducted at 60°C. for a period of time after which the sealed tubes were stored at room temperature. Following the 60°C. interval the presence of the thermal polymer is evidenced by the tacky material on the side of the tube (butadiene layer) and a suspension of white polymer in the aqueous layer. Additional polymerization during the approximately 10 year interval following the 60°C. reaction appears to be negligible. The butadiene layer remains quite fluid, and there is no evidence of popcorn nucleation. The presence of iron or iron oxide produces no changes in the observed products. When opened, a typical tube still contains approximately 70–80% monomer after 10 years.

When benzoyl peroxide is present in the butadiene–water system (iron or iron oxide in the vapor phase) the polymerization at 60°C. leads to a clear, very viscous, tacky polymer, and the water phase again becomes milky with dispersed white polymer. After 61 days at 60°C. no popcorn is present. After standing at room temperature for several years, however, popcorn polymer appears at the water–butadiene interface, the growth extending into both phases. In several experiments popcorn also formed on the glass wool plug and the bottom portion of the iron wire in the vapor phase.

The polymerization of pure butadiene when a sealed tube is allowed to stand undisturbed results in complete conversion to popcorn in approximately one year.[4] These experiments have been confirmed in our laboratory. The polymer is 99.3% insoluble in benzene, and the infrared spectrum is similar to that of popcorn prepared by other methods.[12]

When cobalt metal is placed in the presence of butadiene monomer vapor at 60°C., popcorn polymer formation occurs on the edges of the metal surface in approximately 6 days. This polymer is >99% insoluble in benzene and again shows an infrared spectrum similar to the popcorn formed by other methods.[12]

DISCUSSION

Nucleation in a Heterogeneous System

The mechanism for nucleation proposed is as follows. First, sorption of the butadiene monomer, M, occurs on the cobalt metal surface, [Co]:

$$M_{vapor} + Co \rightarrow M_{surface}\,[Co] \quad (1)$$

Active polymerization is initiated here by either the addition of a monomer molecule from the vapor phase, M_{vapor}, to the sorbed molecule, $M_{surface}$, or, more likely, the addition of two sorbed monomer molecules:

$$M_{vapor} + M_{surface}\,[Co] \rightarrow P[Co] \quad (2)$$

$$M_{surface}\,[Co] + M_{surface}\,[Co] \rightarrow P[Co] \quad (3)$$

Subsequent addition produces a sorbed chain, P[Co], which is now in a position whereby direct reaction of monomer from the vapor phase can occur via hydrogen atom transfer or direct addition to a double bond:

$$P[Co] + M_{vapor} \rightarrow M\text{—}P[Co] \rightarrow P_{branch}\,P[Co] \quad (4)$$

These propagating branch chains, P_{branch}, are essentially perpendicular to the surface. They grow rapidly, and due to their immobility and close proximity they become vulnerable targets for the crosslinking reaction with the resultant formation of the insoluble nucleus:

$$P_{branch}\,P[Co] + P_{branch}\,P[Co] \rightarrow \text{popcorn} \quad (5)$$

This growth mechanism is applicable to the formation of popcorn in any heterogeneous system, including the benzoyl peroxide-catalyzed experiments where popcorn forms on the iron surface in the liquid phase.

The photopolymerization of butadiene reported by Gee produced a nonvolatile, benzene-insoluble polymer on the walls of the reaction vessel. He proposed a mechanism whereby the active polymer reaches the surface from the gas phase where it becomes deactivated to inactive polymer, or a reversible adsorption of butadiene occurs to form a sorption complex which in turn may grow to a fresh molecule of one unit higher complexity, the cycle being repeated until all the polymer is deactivated. This mechanism cannot apply to the case of the cobalt-catalyzed reaction, for here there are no active radicals produced in the vapor phase and the active centers must exist on the sorbed species. The proposed mechanism for the cobalt-catalyzed system, however, is readily adaptable to the case of photopolymerization, for one only needs to postulate the additional reaction possibilities presented by the presence of the mercury-photosensitized species. Experiments now in progress indicate that exposure of butadiene popcorn polymer seed to ultraviolet radiation may activate the seed slightly during the first part of the exposure, but continued exposure produces a deactivation of the seed for the spontaneous growth reaction.

Nucleation in an Apparently Homogeneous System

Pure butadiene when allowed to stand in glass tubes at room temperature will always produce popcorn polymer. We believe this polymerization to be a heterogeneous process, the active nuclei being formed on the glass surface. Since glass is actually a poor catalyst and since the rate of thermal polymerization is very slow at room temperature, the great variation in observed induction times preceding popcorn growth can be explained. The catalytic effect of a glass wool plug has been observed in other experiments.

When a mixture of butadiene and water is heated at 60°C. for various time intervals and is then allowed to stand undisturbed for extended periods of time there is no formation of popcorn polymer, and there is a diminution in the degree of butadiene polymerization to soluble polymer. This result is independent of the presence or absence of iron or iron oxide in either the liquid or vapor phase. If Breitenbach's theory of entanglement of long chains as a sufficient condition for popcorn formation applies, it is difficult to see why no popcorn polymer was initiated in these experiments. Again, the explanation proposed is that the popcorn nucleation phenomenon is a heterogeneous reaction and here the presence of water vapor acts as an effective poison for the active sites which can exist on the glass surface.

When benzoyl peroxide is present along with butadiene and water, the formation of popcorn polymer is observed after a high degree of polymerization is existent in the butadiene layer. Here the active surface is the water–butadiene (mostly polymer) interface, where there undoubtedly exists a higher concentration of short chains and the needed crosslink-producing free-radical species.

If the foregoing assumptions made by the authors are correct, it can be concluded that the formation of butadiene popcorn polymer nucleation occurs in all observed cases as a heterogeneous surface reaction.

SUMMARY AND CONCLUSIONS

Butadiene popcorn polymerization can be initiated by placing cobalt metal in the presence of monomer vapor. Using this system as a model, a mechanism for the formation of the initial popcorn nuclei has been postulated. The reaction is heterogeneous and proceeds by the following steps: sorption of monomer; polymerization of sorbed monomer to form short sorbed chains; branching of the chains via direct addition to the double bonds or by hydrogen atom transfer; crosslinking of the branches due to their close proximity and orientation resulting from the surface attachment; and finally propagation of the nuclei thus produced. The variation in the length of the induction time preceding popcorn formation in a system and the complete lack of popcorn formation in other systems can be attributed to the presence or absence of an effective surface on which the nucleation reaction can occur.

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Synopsis

Butadiene popcorn polymerization can be initiated by placing cobalt metal in the presence of monomer vapor. Using this system as a model, a mechanism for the formation of the initial popcorn nuclei has been postulated. The variation in the length of the induction time preceding popcorn formation in a system and the complete lack of popcorn formation in other systems can be attributed to the presence or absence of an effective surface on which the nucleation reaction can occur.

Résumé

La polymérisation en flocon du butadiène peut être initiée en plaçant du cobalt métallique en présence de vapeur de monomère. En employant ce système comme modèle, on a postulé un mécanisme pour la formation du noyau flo conneux initial. La variation dans la durée du temps d'induction précédant la formation du flocon dans un système et le manque total de formation de flocon dans d'autres systèmes, peuvent être attribués à la présence ou à l'absence d'une surface effective sur laquelle la réaction de nucléation peut avoir lieu.

Zusammenfassung

Popcorn-Polymerisation von Butadien kann durch Einbringen von Cobaltmetall in den Monomerdampf gestartet werden. Mit Hilfe dieses Systems als Modell wurde ein Mechanismus für die Bildung der ersten Popcornkeime aufgestellt. Die Variation der Länge der der Popcornbildung in dem einen System vorangehenden Induktionsperiode und das völlige Ausbleiben der Popcornbildung in anderen Systemen kann auf das Vorhandensein oder Fehlen einer geeigneten Oberfläche für die Keimbildungsreaktion zurückgeführt werden.

Discussion

P. P. Maning (*I.C.I. Ltd., Herts, Great Britain*): I would like to ask Dr. Miller about two points. Firstly, he has formulated the reaction with cobalt metal, is it not more likely that a surface oxide layer is involved? Secondly, can one be sure that 1 part/million or so of oxygen is not present in the butadiene, as this might be sufficient to form hydroperoxides which could cause the popcorn nucleation?

G. H. Miller: Various types of cobalt surfaces have been tested including metal that was reduced *in situ*. Best results were obtained with a piece of cobalt that was freshly fractured (exposed to air). The polymer growth appeared to first form and be concentrated on the edges of the metal specimen. It must be remembered, however, that reproducibility of results varied with the source of Co metal of the same reported purity thus indicating a catalytic effect of something like an oxide layer or trace impurity.

We believe the peroxide content of the butadiene used was negligible. Purity was tested via infrared, ultraviolet and mass spectographic analyses. Gas chromatographic separatism yielded very small amounts of butane and butane impurities.

S. H. Pinner (*B.X. Plastics, Essex, Great Britain*): Can you comment on the structure of popcorn? Do we understand fully why this material is so insoluble? Is there positive evidence for crosslinking in all cases?

G. H. Miller: The insolubility of butadiene popcorn polymer is attributed to the high degree of crosslinking in the structure. There is much evidence for the crosslinking, for a crosslinking agent (divinyl compound) is a prerequisite for popcorn formation.

Popcorn polymer is completely insoluble, but a few per cent of soluble polymer is usually present and this can be removed by extraction.

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Zur Kenntnis der Bildung inhomogener, wachstumsfähiger Polymer (Popcorn Polymers)

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Die Bildung inhomogener Polymerisate bei der Polymerisation von Divinylverbindung ist eine schon lange bekannte Erscheinung.[1–3] Systematische Untersuchungen am System Styrol–Divinylbenzol brachten einige wichtige Erkenntnisse auf diesem Gebiet.[4–6] In der vorliegenden Arbeit wird versucht vor allem die chemischen Grundlagen zu erweitern.

Styrol–*p*-Divinylbenzol

Die Versuche im System Styrol–*p*-Divinylbenzol hatten das Ergebnis, dass eine von den Versuchsbedingungen (Polymerisationstemperatur und Starterkonzentration) abhängige gut definierte optimale Konzentration der Divinylverbindung für die Bildung inhomogener Polymerisate besteht. Weiter haben diese Polymeren die bemerkenswerte Eigenschaft, in reinem monomeren Styrol weiter zu wachsen. Die zuwachsende Menge Polymeres kann sehr grosse Beträge annehmen und liefert Polymerisate die ihrer Zusammensetzung nach praktisch dem aufgewachsenen Monomeren entsprechen, ihren Eigenschaften nach aber typische inhomogene Polymerisate sind.

Styrol–Methacrylsaureänhydrid

Die chemische Spezifität der Bildung inhomogener Polymerisate wird dadurch gezeigt, dass z.B. Methacrylsäureanhydrid als Divinylkomponente mit Styrol keine solchen Polymeren bildet.[7] Wie Tabelle I zeigt liefert es einen analogen stufenweisen Vernetzungsmechanismus wie *p*-Divinylbenzol.

An den bei hohen Umsätzen (ca. 90%) erhaltenen Polymeren wurde der Quellungsgrad in Benzol bestimmt. Er zeigte die zu erwartende Abhängigkeit von der Methacrylsäureanhydridkonzentration im Polymerisationsansatz (Tabelle II).

Obgleich in System Styrol–*p*-Divinylbenzol in diesem Quellungsgradbereich das Gebiet der Bildung inhomogener Polymerisate liegt, tritt diese Erscheinung hier nicht auf; alle Polymerisate haben die normale glasklare Beschaffenheit.

TABELLE I

Polymerisation im System Styrol–Methacrylsäureanhydrid. 2×10^{-3} Mole Benzolperoxyd pro Mol Styrol bei 50°C.

Polymerisationdauer, Stdn.	Methacrylsäureanhydrid, Mole/Mol Styrol	Umsatz,%	$[\eta]$, ml/g
1	0,002	1,02	0,11
2	0,002	2,00	0,15
3	0,002	2,93	0,26
5	0,002	5,68	Unlöslich
8	0,002	12,4	Begrenzt quellbar
1	0	0,80	0,11

TABELLE II

Quellungsgrad Q von Styrol–Methacrylsäureanhydridcopolymeren. Polymerisation bei 50°C mit 2×10^{-3} Molen Benzoylperoxyd pro Mol Styrol: Poylmerisationsdauer 65 Stunden

Methacrylsäureanhydrid im Polymerisationsansatz, Mole/Mol Styrol	Löslicher Anteil, %	Quellungsgrad des unlöslichen Anteils in Benzol
0,002	20,3	9,6
0,006	18,7	5,4
0,010	18,9	4,4
0,014	14,3	3,9
0,020	13,8	3,3
0,040	7,4	2,3

Acrylsäureester

Eine prinzipielle Erweiterung erfuhr das Gebiet der inhomogenen Polymerisate durch die Beobachtung, dass Acrylsäuremethylester bei niedrigen Starterkonzentrationen einer solchen Polymerisation fähig ist.[8] Etwas abeschwächt ist die Erscheinung schon bei Äthylacrylat, während bei *n*-Butylacrylat nur mehr die normalen, glasigen Polymeren auftreten. Die Tendenz zur Bildung von inhomogenen Polymerisaten nimmt bei Acrylsäuremethylester und Acrylsäureäthylester mit fallender Starterkonzentration zu. Bei 20°C und mit Benzoylperoxyd als Starter kommt es bei Starterkonzentrationen grösser als 10^{-3} Mol pro Mol Methylacrylat zur Bildung der normalen, glasigen Polymeren, mit 10^{-4} Mol und noch stärker mit 10^{-5} Molen Benzoylperoxyd pro Mol Monomeres wird inhomogene Polymerisation beobachtet. Beim Äthylacrylat liegt die Konzentrationsgrenze um nicht ganz eine Zehnerpotenz tiefer.

n-Butylacrylat–Glykoldimethacrylat

Beim Butylester benötigt man schon wieder eine Divinylkomponente. Als solche wurden mit bestem Erfolg Glykoldimethacrylat verwendet.[9]

TABELLE III

Bildung von inhomogenen Polymerisaten im System *n*-Butylacrylat–Glykoldimethacrylat. Polymerisation mit 0,1 Mol % Azoisobutyronitril bei 40°C durch 6 Tage

Glykoldimethacrylat, Mol-%	Inhomogenes Polymeres tritt auf	
	An Grenze zur Gasphase	In der Flüssigkeit
1,4	Wenig	Keines
2,6	Wenig	Wenig
4,3	Stark	Stark
6,3	Stark	Keines
10,6	Keines	Keines

Wie beim System Styrol–*p*-Divinylbenzol besteht ein optimaler Zusammensetzungsbereich für die Bildung inhomogener Polymerer (Tabelle III).

Glykoldiacrylat

Ausgezeichnet wirksam in der gleichen Richtung ist Glykoldi-acrylat als Vernetzer. Diese Verbindung neigt auch schon für sich allein, ohne Starterzusatz zur inhomogenen Polymerisation. Ein Verlust der Fähigkeit inhomogene Polymerisate zu bilden tritt beim Übergang vom Methylacrylat zum Methylmethacrylat auf. Dieser Umstand spricht für die Wichtigkeit des tertiären Wasserstoffatoms im Methylacrylat für diese Erscheinung, was wieder auf die Bedeutung einer Übertragungsreaktion mit dem Polymeren hinweist. Tatsächlich ist ja bei häufigerem Auftreten einer solchen Übertragungsreaktion und bei gleichzeitigem Kettenabbruch durch Radikaladdition die Bildung vernetzter Systeme auch bei reinen Monovinylverbingungen möglich und damit eine Voraussetzung für das Auftreten inhomogener Polymerer gegeben.

Wachstum inhomogener Polymerisate

Styrol. Besonders eindrucksvollist, wie schon erwähnt die Wachstums fähigkeit der inhomogenen Polymerisate. Eine grosse Zahl dilatometrischer Messungen über das Wachstum von inhomogenen Styrol–*p*-Divinylbenzolpolymeren[10] ergab einen grossen Bereich von Wachstumsgeschwindigkeiten und zwar bestand eine deutliche Abhängigkeit von der Dichte der Polymeren. Polymere mit sehr dichter Struktur, wie sie besonders in engen Reaktionsgefässen erhalten werden können, wachsen langsam, während locker gebaute Polymere, die besonders bei Wachstum in die Gasphase entstehen, rasch wachsen. Allgemein nimmt die Wachstumsgeschwindigkeit am Anfang mit der Zeit rasch zu, erreicht einen Maximalwert und klingt dann langsam ab (Tabelle IV). Sie fällt aber auch nach langer Zeit nicht auf Null ab.

Im Intervall von 13 bis 24°C nimmt die Wachstumsgeschwindigkeit mit der Temperatur stark zu, entsprechend einer scheinbaren Aktivierungsenergie von fast 40 kcal/Mol. Wenn auch diese Zahl sicher keine einfache

TABELLE IV
Wachstum von inhomogenen Styrol–*p*-Divinylbenzolcopolymeren in reinem Styrol bei Keime

Wachstumsdauer, Stdn.	Aufgewachsene Menge Styrol, g	
	I[a]	II[b]
6	0,006	0,006
18	0,062	0,270
44	0,577	1,180
69	0,945	1,750
91	1,310	2,960
123	1,610	2,35

[a] I mit 1,63% DVB; 0,0517 g.
[b] II mit 1,74% DVB; 0,0653 g.

physikalische Bedeutung hat, so zeigt sie doch klar genug, dass für das Wachstum nicht präformierte Radikale massgebend sind, sondern diese erst im Laufe des Prozesses gebildet werden.

***n*-Butylacrylat.** Es wurde schon früher gezeigt, dass bei solchen Wachstumsversuchen die Radikalen im Monomeren nach den bekannten Mechanismen gebildet werden, durch Reaktion mit dem inhomogenen Keim an diesem fixiert werden und durch weitere Monomeraddition dessen Massenzunahme bewirken. Es ist daher nicht verwunderlich, dass Keime aus reinem inhomogenen Polyglykoldiacrylat sich durch besondere Wachstumsfähigkeit auszeichnen. Aber auch durch Aufwachsen entstandene Polymere, die praktisch keine Doppelbindungen mehr besitzen sind noch

Abb. 1. Wachstum in *n*-Butylacrylat, Anfangszustand.

wachstumsfähig. Hier sind es wahrscheinlich wieder Übertragungsreaktionen mit dem inhomogenen Material und in manchen Fällen auch bloss Kettenverschlingungen, die für das Keimwachstum verantwortlich sind. Eine gross Zahl von Wachstumsversuchen wurde nun in *n*-Butylacrylat

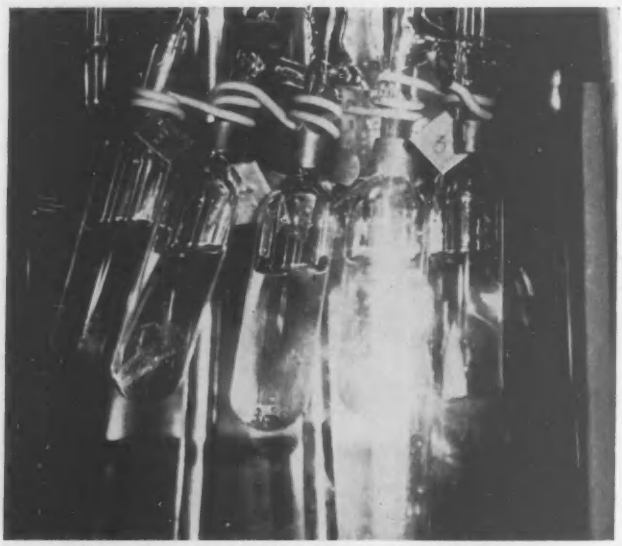

Abb. 2. Wachstum in *n*-Butylacrylat, Dauer 3 Stunden.

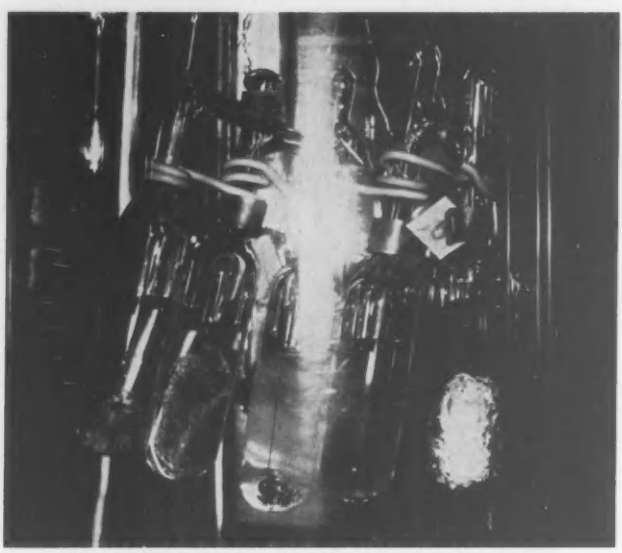

Abb. 3. Wachstum in *n*-Butylacrylat, Dauer 8 Stunden.

als Monomerem durchgeführt.[9] Hier treten schon rein äusserlich recht verschiedenartige Wachstumserscheinungen auf, die zum grossen Teil wahrscheinlich auf den recht verschiedenen mechanischen Eigenschaften von Poly-*n*-butylacrylat gegenüber von Polystyrol beruhen.

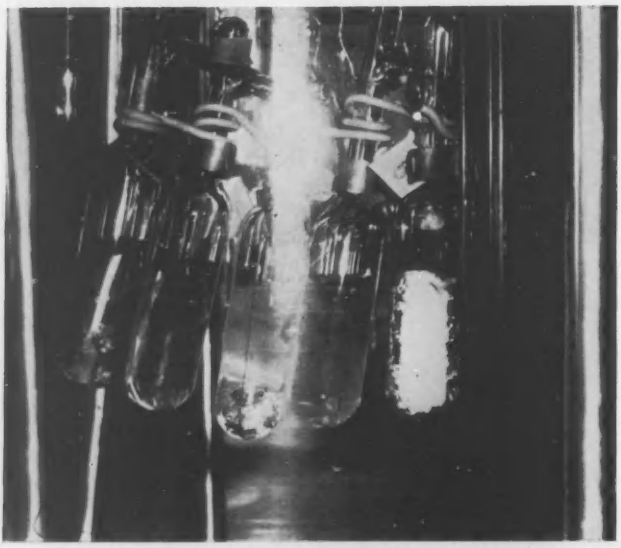

Abb. 4. Wachstum in *n*-Butylacrylat, Dauer 13 Stunden.

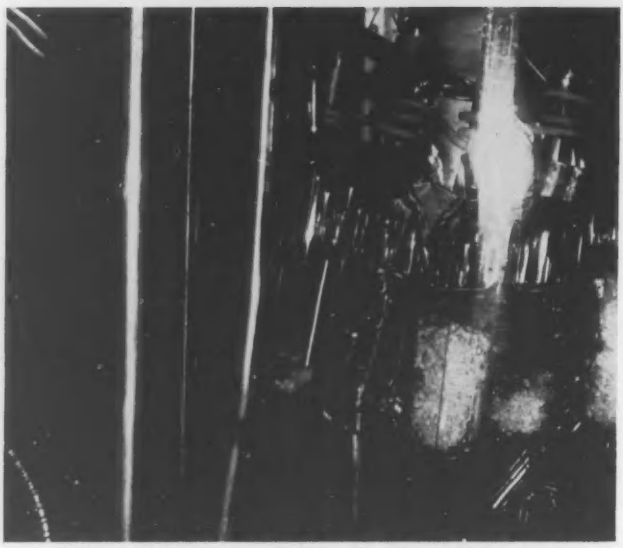

Abb. 5. Wachstum in *n*-Butylacrylat, Dauer 25 Stunden.

Die Abbildungen 1–5 geben ein Bild des Wachstums einiger inhomogener Polymerisate in reinem *n*-Butylacrylat bei 20°C. Es wurden nebeneinander fünf Versuche ausgeführt. Am Anfang des Versuches befanden sich in jedem Gefäss 10 ml *n*-Butylacrylat und eine kleine Menge Keimmaterial und zwar von links nach rechts: in Gefäss 1 (0,13 g) und 2 (0,16 g) ein inhomogenes Material, das aus einem *n*-Butylacrylat–Glykoldimethacrylatgemisch an der Grenze zur Gasphase entstanden war und blättrige Struktur besass; in Gefäss 3 inhomogenes Polymeres (0,40 g) aus dem gleichen Ansatz, aber in der flüssigen Phase gebildet, mit körniger Struktur, in Gefäss 4 ein inhomogenes Glykoldiacrylatpolymeres (0,39 g) in der Gasphase entstanden und in Gefäss 5 ein ebensolches (0,39 g), das sich bei der Destillation von Glykoldiacrylat in der Kolonne gebildet hatte. Abbildung 1 zeigt das Anfangsstadium; Abbildung 2 das Wachstum nach 3 Studen; hier ist besonders das starke Wachstum in Gefäss 2 sowie die Bildung der Wachstumsschichten in Gefäss 3 bemerkenswert. Abbildung 3 Wachstum nach 8 Stunden: gut sichtbares Wachstum in 1, der Keim in 2 hat schon fast das ganze Monomere durchwachsen, in 3 ist das Wachstum deutlich, in 5 sehr stark nur in 4 gering. In Abbildung 4 (nach 13 Stunden) ist auch in 4 Wachstum sichtbar; besonders bemerkenswert 5, wo auf dem inzwischen in ein Gel umgewandelten Monomeren ein getrenntes Wachstum beginnt, wahrscheinlich durch Spuren von Keimmaterial verursacht die sich im oberen Teil des Gefässes befanden. Nach 25 Stunden (Abb. 5) ist auch das Wachstrum in 3 und 4 recht ausgeprägt geworden. Es wird durch diese Bilder recht deutlich, dass die Wachstumserscheinungen von den in Styrol beobachteten stark verschieden sind und dass die Struktur des Keimmaterials auf Geschwindigkeit und Charakter des Wachstums einen tiefgehenden Einfluss besitzt. Die Wachstumserscheinungen erweisen sich als qualitativ reproduzierbar und es erscheint lohnend die Verhältnisse auch quantitativ zu untersuchen. Nach unseren bisherigen Versuchen scheint das Wachstum eines inhomogenen Polymeren in einem Monomeren auch die Polymerisationsgeschwindigkeit des Monomeren in homogener Phase zu erhöhen. Die aufgewachsenen Polymeren zeigen das mechanische Verhalten der entsprechenden normalen Polymeren. Aufgewachsenes Polystyrol ist ein hartes, starres Material, aufgewachsenes *n*-Butylacrylat eine weiche kautschukartige Substanz.

Der grössere Überblick, den wir besonders mit der Einbeziehung der Acrylsysteme gewonnen haben, hat auch unsere Ansicht über den Bildungsmechanismus der inhomogenen Polymerisate beeinflusst. Nach den Untersuchungen an Styrol–Divinylbenzolsystemen neigten wir dazu, mechanische Spannungen, die durch die Kontraktion während der Polymerisation in solchen Systemen recht augenfällig auftreten, als die unmittelbare Ursache anzunehmen. Nach unserer jetzigen Meinung ist die Ursache aber eine mehr chemische. Durch die gleichzeitige Anwesenheit einer grossen Anzahl wachsender Radikalzentren in einem kleinen Volumen des vernetzten Gels kommt es zu einem raschen Verbrauch des Monomeren, der durch die Nachlieferung durch Diffusion nicht gedeckt werden kann.

Dadurch entstehen Hohlräume, die das typische Aussehen der inhomogenen Polymeren verursachen. Das bevorzugte Auftreten der inhomogenen Stellen an Phasengrenzen ist auf Grund dieser Vorstellung leicht verständlich. Das Ziel unserer nächsten Arbeiten ist es, diese Arbeitshypothese einter eingehenden experimentellen Überprüfung zu unterziehen.

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Zusammenfassung

Die Bildung inhomogener Polymerisate in verschiedenen Vinyl-Divinylsystemen wird untersucht. Neben Styrol–*p*-Divinylbenzol erweist sich besonders das System Butylacrylat–Glykoldimethacrylat als recht interessant. Die Bildung von Popcornpolymeren ist eine reproduzierbare, an einen bestimmten Mischungsbereich des Systems gebundene Erscheinung. Die Wachstumserscheinungen in verschiedenen Monomeren werden untersucht. Eine Charakterisierung der Polymeren wird durchgeführt.

Synopsis

The formation of popcorn polymers in various vinyl divinyl systems has been studied. Besides the pair styrene–divinylbenzene the system butylacrylate–glycoldimethacrylate is investigated in more detail. Popcorn polymers are formed quite reproducibly in a certain range of composition. The growth of preformed popcorns in different monomers has been studied. Characteristic properties of the polymers are presented.

Résumé

La formation de polymères hétérogènes au départ de systèmes vinylique-divinylique a été examinée. Outre le couple styrène-*p*-divinylbenzène, c'est le système acrylate de butyle–diméthacrylate d'éthylèneglycol qui est le plus intéressant. La formation de graines polymériques est un phénomène reproductible, et lié à un rapport de composition déterminé. Les phénomènes de croissance sont examinés avec divers monomères. Les polymères ont été caractérisés.

Discussion

A. Chapiro (*C.N.R.S., Bellevue, S. et O. France*): Je voudrais faire une remarque concernant le mécanisme de la polymérisation "popcorn". Toute interprétation de cette réaction doit expliquer les phénomènes suivants: (*1*) nucléation mal reproductible; (*2*) formation d'un polymère réticulé (gel); (*3*) courbes de conversion auto-accélérées; (*4*) réinitiation par des germes de popcorn.

Or tous ces caractères ont été bien expliqués il y a quelques années par Medvedev et coll. qui ont montré que les germes étaient des particules de polymère reticulées formées au hasard au cours de la réaction. La réaction se poursuivait ensuite par un mécanisme d'initiation "mécano-chimique," Les particules de gel gonflent dans le monomère et ce gonflement conduit à la rupture de chaînes polymèriques, donnant ainsi naissance à des radiaux supplémentaires. Ceci explique en particulier les courbes auto-accélerées et la possibilité de réamorcer la réaction avec des germes de popcorn (polymère reticulé). Les très beaux clichés au microscope polarisants obtenus par le Prof. Breitenbach mettent en evidence les fortes tensions qui existent dans le gel de popcorn et qui sont responsables de la rupture des chaînes.

H. A. Dieu (*Université de Liège, Belgium*): In relation with the question of Dr. Pinner concerning Dr. Miller communication, I would like to have the comments of Dr. Breitenbach on the solubility of his polymers.

S. H. Pinner (*B. X. Plastics Ltd., Essex, Great Britain*): What are the solubility characteristics of first and second popcorn? Have any gel fraction and crosslink density measurements been carried out?

A. Pravednikov (*Karpov Institute, Moscow, U.R.S.S.*): Eight years ago in our laboratory it was found that in the case of a nucleus obtained from labeled chloroprene, the polymerization of nonlabeled chloroprene followed with the formation of polymer, characterized by an absolutely homogeneous distribution of radioactivity in all the volume of the sample. Since the popcorn polymer has a network structure, such a homogeneous distribution could be achieved only following the rupture of some macromolecules of the radioactive nucleus. Consequently we assume that popcorn polymerization is actually a mechanochemical process.

B. Wright (*Shell Chemical Co., Manchester, Great Britain*): In how far does the rate of growth of popcorn depend on the type of nuclei?

J. W. Breitenbach: A more intimate knowledge of the structure of inhomogeneous polymers has been obtained by microscopy of thin sections (10μ) of inhomogeneous styrene–*p*-divinyl-benzene copolymers in polarized light. These polymers always contain a portion of optically anisotropic material, also after growing to more than one hundred times the original weight in pure styrene. This optical anisotropy is enhanced by treating the material with boiling *n*-heptane during several hours (annealing) but the x-ray patterns remain amorphous. Obviously the popcorn polymers contain regions of higher order than the normal glass-like material but as a consequence of their atactic character they are not able to cristallize. This order seems to be due to the growth of network bound chains in the immediate neighbourhood of net-chains extended by swelling. Earlier experiments, (J. W. Breitenbach, H. Preussler, H. Karlinger, *Monatsh. Chem.*, **80**, 150 (1949)) have clearly shown that there is no "mechanochemical" production of free radicals by swelling and rupture of the crosslinked network. So the styrene–*p*-divinylbenzene popcorn did not grow in styrene containing phenanthraquinone as an inhibitor during an extended period, but after photochemical destruction of the quinone growth occured. Similarly growing of the popcorn in vinylacetate could only be observed when the monomer contained an initiator (benzoylperoxide).

This is further confirmed by the fact that pure methylacrylate popcorn does not grow markedly in styrene but does grow in *n*-butylacrylate. This popcorn does not contain any C—C double bonds and therefore the production of growing centers on the polymer must proceed by chain transfer and not by addition. In this respect the more reactive polyacrylate radicals are better suitable than polystyrene radicals.

It must be concluded that only the normal chemical reactions (addition of free radicals to pendant double bonds, chain transfer) are responsible for the formation of network-bound free radicals.

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Radiation-Induced Ionic Polymerization of Styrene: Effects of Additives

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INTRODUCTION

By irradiating at low temperatures in the presence of suitable solvents of high dielectric constant, such as dichloromethane, styrene can be polymerized via an ionic mechanism.[1-3]

As in the case of the radiation-induced ionic polymerization of isobutene,[4,5] it has been found that yields of polymer can be greatly enhanced by the addition before irradiation of small quantities of finely divided inorganic oxides.[2] Our previous work established the conditions required for the ionic polymerization of styrene, and showed how the rate of polymerization varied with dose rate and styrene concentration, with and without solid additives.

Results with only two surface-modified Hi-Sils appeared to confirm our preliminary theory concerning the mechanism of the enhancement of yields.

In the present work, the range of surface-modified silicas has been extended. The effect of an electron-trapping agent on the cationic reaction has been studied, and changes in the conductivity of the polymerizing solutions have also been investigated.

EXPERIMENTAL

Purification of Reagents

BDH Lab-reagents grade styrene and dichloromethane were purified as in our previous work.[2] Both reagents were stored over bright sodium wire until required. Tetracyanoethylene (Eastman Kodak) was used direct.

Additives

Surface-modified Aerosils were not out-baked before use due to the unknown stability of the organic groups. All additives were, however, desiccated over sodium in a reaction tube for one week.

Reagents were introduced into the reaction tubes by pipett, through a spiral of sodium wire. This procedure gave results identical with those

obtained when the solutions were introduced into the tubes by distillation on the vacuum line.

All samples were thoroughly degassed by freezing–evacuating–melting cycles until no gas bubbles were seen.

Irradiation

Our 2000-curie Co^{60} gamma source was used. The samples were irradiated in standard Pyrex tubes maintained at −78°C. in a solid CO_2–ethanol bath.

Yields of polymer were determined by precipitation of the polystyrene with cold methanol, filtering, drying, and weighing. In the series with solid additives present, the total solid (after addition of methanol) was weighed, and weight of polymer determined by difference. The measurements were confirmed by dissolving the polystyrene from the additive with dichloromethane, evaporating to dryness, and weighing.

Molecular Weights

These were determined from intrinsic viscosity measurements in benzene solution at 25°C. in an Ubblehode viscometer. The relation,[6] $[\eta] = 2.34 \times 10^{-4} \bar{M}_v^{0.69}$ and $\bar{M}_v = 1.85\bar{M}_n$ were taken as being representative of the molecular weight range covered.

$G_{\text{initiation}}$ values were calculated for energy absorbed in the styrene only (no energy transfer) and for all energy absorbed by solution and additives (100% energy transfer).

RESULTS

Previous work[2] has provided the following information on the ionic polymerization of styrene.

In the absence of solid additives, the rate of polymerization varies directly with the radiation intensity ($dp/dt \propto I^{1.0}$), the molecular weight varies as the square root of the styrene concentration ($\bar{M}_n \propto C)^{0.5}$, and trace quantities of water inhibit the reaction due to increased termination. With Aerosil present, the rate of polymerization varies as $I^{0.5}$, and molecular weight varies as $C^{0.125}$, indicating that preferential absorption of the styrene ion takes place on the additive, and that neutralization of the growing cationic chains occurs by separate ionizations. Surface modified Hi-Sils, which gave large numbers of stabilized radicals,[7] did not enhance the yield of polymer.

In the present work, a much wider range of surface-modified silicas was investigated, the substrate in all cases being Aerosil of 230 $m.^2/g.$ surface area, with known proportions of surface silanol groups replaced to give organic-silyl groups. The results obtained are shown in Table I. In each case the optimum quantity of additive was taken so that the mixture remained fluid with no supernatant liquid.

TABLE I
Solution of Styrene in Dichloromethane (1:3 v/v) Irradiated at −78°C. for 50 Hr. at 40 Krad/hr.

Modifying group	Active silanol groups replaced, %	Weight of additive, g./4 ml.	Yield, %/Mrad	Molecular weight $M_n \times 10^{-3}$	$G_{initiation}$ No energy transfer	$G_{initiation}$ 100% energy transfer
No additive	—	—	7.5	30	2.4	0.45
Untreated	—	0.153	25	42	5.8	1.05
Ethyl	60	0.7032	18	53	3.4	0.56
Allyl	50	0.7113	17.5	52	3.4	0.56
Butyl	50	0.7043	13.5	50	2.7	0.44
Butyl	100	0.707	10.5	42	2.5	0.44
Diethylene glycol	50	0.7458	14	48	2.9	0.47
Lauryl	50	0.706	8	35	2.3	0.38
Benzyl	100	0.705	1.3	25	0.52	0.085

The surface-modified Aerosils have bulk densities much greater than the untreated Aerosils, so correspondingly higher weights are needed to equal the total bulk of solution.

It can be seen that by increasing the surface coverage with a particular organic group (butyl), the yield of polymer is decreased, mainly due to a decrease in the molecular weight.

Increasing the length of the modifying species, as in the case of the lauryl derivative, decreases the yield in a similar fashion. With all the alkyl and allyl deviations however, there is an enhancement of yield observed above that which could be attributed to energy transfer from the additive.

In the case of the benzyl derivative, a considerable reduction in yield is noted, which is mainly due to decreased initiation.

Addition of Electron-Trapping Agent

In the absence of additives, the dose rate dependance of rate of polymerization shows that the growing chains are terminated by the electron initially removed to give a positive styrene ion. Some polymerizations were therefore conducted with a strong electron-trapping agent present.

TABLE II
Styrene–CH_2Cl_2 (1:1 v/v) Polymerized at −78°C. for 50 Hr. at 40 Krad/hr.

Additive	Yield %/Mrad	Molecular weight $M_n \times 10^{-3}$	$G_{initiation}$ No energy transfer	$G_{initiation}$ 100% energy transfer
None	2.8	39	0.69	0.299
TCNE	2.2	32	0.66	0.285
Aerosil	16	47	3.3	1.22
Aerosil + TCNE	14	41	3.3	1.22

The agent used, tetracyanoethylene (TCNE) was added in excess of that required to eliminate all electrons released, based on the $G_{initiation}$ value, the concentration being from 0.5 to 1.5 g./l. of 1:1 (v/v) styrene–dichloromethane solution. A summary of these results is given in Table II.

Thus, a slight decrease on yield was found, due almost entirely to a decrease in molecular weight.

Conductivity Measurements

Conductivity measurements were made on the polymerizing solutions, which had been dried and degassed as before, using a simple d.c. cell with 1-cm. square platinum electrodes set 1-cm. apart. In each case, the resistance of the cell was ohmic from 65 to 455 v.

The main feature which arises from these results (Table III) is that TCNE greatly increases the conductivity of styrene–CH_2Cl_2, and this has also been found to apply to CH_2Cl_2 alone. However, when untreated Aerosil is present, the Aerosil has little effect on the conductivity, as does Hi-Sil modified with diethoxyvinyl silyl groups, but when TCNE is present, it can be seen that with untreated Aerosil, there is little change, but with the surface-modified Hi-Sil, a fourfold increase in conductivity is found. In all cases the conductivity increases with dose rate, but in a somewhat complex manner, and preliminary investigations at 500 krad/hr. indicate that a limiting value for the conductivity may be reached.

TABLE III
Conductivity of Styrene–CH_2Cl_2 (1:1 v/v) at −78°C.

	Conductivity, mho × 10^{11}					
Dose rate, krad	No additive	TCNE	Aerosil	Aerosil + TCNE	Surface-modified	Hi-Sil + TCNE
0	6.4	100	5.7	11	9.3	38
2.5	9.9	110	—	13	11.7	41.5
12	11	114	13	15	12.3	43.1
30	14	125	15	17	15.1	47.6

DISCUSSION

The present work appears to confirm our previous theory that the enhancement of the radiation-induced polymerization of styrene by solid additives occurs via an ionic mechanism on or near the surface of the additive. The enhancement found with 100% surface-modified Aerosils, at first surprising, becomes clear when one considers that the 100% refers to the replaceable silanol groups.[8] In our previous work, the out-baking to which the Aerosil was subjected would not have removed all of these groups so that there was still water absorbed on the silica surface. It appears therefore that the styrene ions are stabilized on the silicon oxide groups, which do not normally absorb water molecules; adsorption isotherm data of surface areas gained from BET (nitrogen) and water vapor absorption

and infrared measurements show that the water vapor surface area is much less than the BET area.[9] That increasing the percentage modification decreases the yield would then be due to steric effects of the organic radicals blocking potential stabilization sites. This is also indicated by the much greater reduction in yield when a very long radical (lauryl) is present. When a benzyl-substituted Aerosil was used, a diminuation of yield was found. This would be due to a combination of steric effects (which would not reduce the yield below the value with no additive present) and possibly due to the highly resonant benzene structure acting as an energy sink and so reducing ionization of the styrene; this is indicated by the greatly reduced $G_{\text{initiation}}$ value.

The effect of TCNE on the ionic polymerization of styrene shows very little beyond that the styrene ion is apparently a much better electron trapping agent than the TCNE.

The conductivity measurements are not open to precise evaluation, since the mechanism of conductance in chlorinated solvents is not clearly understood, although it has been suggested that the mobile species is ionic rather than electronic.[10]

The effect of styrene appears to be only to reduce the conductivity of the dichloromethane. The role of TCNE in conduction would probably be that of a highly polarizable impurity, greatly increasing conductivity. When Aerosil was present, no such increase in conductivity was observed, and although the solution was colored, it seems likely that most of the TCNE was adsorbed onto the silica surface. This is confirmed by the results with a surface modified silica, when TCNE was not absorbed, and produced a large increase in conductivity.

It is hoped in the near future to investigate the yield enhancing properties of surface-modified Aerosils with a much wider range of known surface coverages.

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Synopsis

When styrene in dichloromethane solution is irradiated at −78°C., the resulting polymerization occurs via an ionic mechanism. We have previously shown that the

yields in this reaction can be greatly enhanced by the addition of finely divided solids such as Aerosil. In the present work, the additives studied include a number of silica powders whose surfaces have been modified by the replacement of hydroxyl groups by alkyl, allyl, and aryl groups. It has been found that the "catalytic power" of these silicas can be correlated with the nature and number of substituted groups. Although the polymerization is cationic in character, the presence of excess electron trapping material (tetracyanoethylene) causes a diminuation of yield. Electrical conductivity measurements on the polymerizing solution, in the presence and absence of additives, have been made to clarify the proposed reaction mechanism.

Résumé

Lorsqu'on irradie le styrène en solution dans le dichlorométhane a −78°C, il se produit une polymérisation par un mécanisme ionique. Nous avons montré précédemment que les rendements pouvaient être considérablement augmentés par l'addition de solides finement divisés tel que l aérosil. Dans le présent travail, des études complémentaires comprenant un certain nombre de poudres de silice dont les surfaces ont été modifiées en remplaçant des groupements hydroxyles par des groupements alcoyle, allyle, et aryle. On montre que le pouvoir catalytique de ces silices peut être mis en corrélation avec la nature et le nombre des groupes substituants. Bien que la polymérisation soit de caractère cationique la présence des matériaux à excès d électrons (tétracyanoéthylène) provoque une diminution du rendement. Les mesures de conductivité électrique de solutions en cours de polymérisation en absence et en présence d'additifs ont été effectuées pour clarifier les mécanismes de réaction proposés.

Zusammenfassung

Bei Bestrahlung von Styrol in Dichlormethanlösung bei −78°C tritt Polymerisation nach einem ionischen Mechanismus ein. Es wurde schon früher gezeigt, dass die Ausbeute bei dieser Reaktion durch Zusatz fein verteilter Festkörper, wie Aerosil, stark erhöht werden kann. In er vorliegenden Arbeit werden als Zusatz eine Anzahl von Kieselsäurepulvern untersucht, deren Oberfläche durch Ersatz der Hydroxylgruppen durch Alkyl-, Allyl-, und Arylgruppen modifiziert wurde. Es zeigte sich, dass eine Korrelation der katalytischen Fähigkeit dieser Substanzen zur Natur und Zahl der substituierten Gruppen aufgestellt werden kann. Obgleich die Polymerisation kationischen Charakter besitzt, verursacht die Gegenwart eines Überschusses eines elektronenbindenden Stoffes (Tetracyanäthylen) eine Verringerung der Ausbeute. Zur Aufklärung des Reaktionsmechanismus wurden elektrische Leitfähigkeits-Messungen an der polymerisierenden Lösung in Gegenwart und Abwesenheit von Zusätzen ausgeführt.

Discussion

S. H. Pinner (*B. X. Plastics Ltd., Essex, Great Britain*): I fail to understand the distinction drawn between (2) electron trapping on the solid additive surface and (3) stabilization of the growing chain on the solid surface. If the propagation proceeds via cations, the electron trapping by the solid surface will enable it to act as a gegen-ion, thereby stabilizing the growing chain end. How else may the cationic active center be stabilized by the surface?

The radiation induced polymerization of isobutene was described by us as being only in part heterogeneous. The most plausible explanation for the absence of a conventional gegen-ion, is that the isotactic carbonium ion can grow during the period between loss and recapture of the electron. The solid surface merely seems to delay the time intervening before electron recapture. The solid surface must be in the vicinity of the growing chain and be effective in this way. Does the proposed mechanism of styrene polymerization differ eventually from this idea?

J. Morris: Concerning the difference between electron trapping by the solid additive,

TABLE IV

	ST. at −78°C.		
	R_p(mol./1 hr.)	DP	R_p/DP
CCl_3H	0.90×10^{-3}	220	4.0×10^{-6}
CS_2	0.50×10^{-5}	230	2.2×10^{-6}
$C_6H_5CH_3$	—	—	—
$C_6H_5C_2H_5$	—	—	—
C_2H_5I	0.07×10^{-3}	13	5.4×10^{-6}
CH_2Cl_2	5.90×10^{-3}	800	9.1×10^{-6}
C_2H_5Br	1.75×10^{-3}	210	9.3×10^{-6}
CH_3Cl	3.30×10^{-3}	560	6.0×10^{-6}
$C_2H_5NO_2$	—	—	—

and stabilization of the growing cationic styrene chain, I think that our disagreement is based mainly on a difference of definition.

As I understand the theory of electron trapping is where in fact the electron concerned is that one which is initially removed from the styrene cation; the polymerization occurs in the liquid phase and the termination rate is reduced because the electrons (or negative terminating species) are adsorbed by the solid additive.

In the present work, I think that it is the growing cationic chain which is adsorbed on the solid and hence is statistical against termination. This would appear to be confirmed by the effects with the surface treated aerosils and by the lack of effect of TCNE.

S. Okamura (*Kyoto University, Japan*): I have two comments. The first is the importance of the effect of solvent which is adsorbed on the surface of the powder of additive. Table IV shows that the solvent affects the rate of propagation, but not the initiation.

The second point is the possibility of electric-conductivity measurements in the irradiated solid crystal. Under γ-irradiation, the electric conductivity increases in the case of the polymerizable cyclic compounds (e.g., β-propiolactone and trioxane), but no differences can be obtained in the case of nonpolymerizable cyclic compound like caprolactone.

C. S. Chen (*American Cyanamid Co., Stamford, Conn.*): I have two comments to make. First I presume that Dr. Morris is familiar with our work on the low temperature polymerization of styrene and its derivatives [*J. Polymer Sci.*, **58**, 389 (1962)]. When styrene was polymerized at its melting point, where crystalline styrene was present in liquid styrene, it was observed that there was an increase both in rate and molecular weight and we have concluded that this was due to a decrease in termination. Here the solid additive was the crystalline styrene monomer itself. Second, in regard to Prof. Okamura's comment, Mr. R. L. Webb in our laboratory reported in the *International Symposium on Application of Radiation in Polymerization and Grafting*, Columbia, Ohio, Nov. 1962, and published in the proceedings, that he has found solvent effects, such as Prof. Okamura just mentioned, in the polymerization of butadiene at low temperatures.

S. Munari (*Istituto di Chimica Industriale, Genova, Italy*): It is necessary to take into account the following points in order to furnish a correct interpretation of the influence of this additive.

(*1*) Aerosil is a commercial product so it is very important to take into account the impurities connected with the fabrication history.

(*2*) The hydroxylic groups on the surface of the powdered additives play a fundamental role in all the phenomena.

(*3*) The electronic structure of the surface must play also a very important role in view of the variation of acidity on the surface.

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Polymérisation Radiochimique de l'Isobutène en Présence d'Additifs Solides

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L'accroissement de vitesse de polymérisation observé en présence d'additifs solides sous irradiation peut avoir deux origines principales. La prèsence d'une surface peut modifier le mécanisme de la réaction en changeant le déroulement d'une ou plusieurs étapes élémentaires, et même parfois la nature des porteurs de chaîne. Le solide peut également transférer au monomère l'énergie qui lui est fournie par les radiations et, par conséquent, augmenter la vitesse d'une étape élémentaire endothermique, comme l'initiation de chaîne. Le premier type d'influence a été mis en évidence dans le cas de la polymérisation de l'éthylène,[1] le second pour des réactions non en chaîne.[2-4]

Notre travail est consacré à l'étude de la polymérisation de l'isobutène initiée par rayonnement γ en présence de différents solides. L'isobutène conduit à des polymères de masse moléculaire élevée en présence de certains initiateurs de réaction cationique.[5] La polymérisation cationique peut également être initiée à basse température dans l'ultra-violet lointain, par des photons dont l'énergie est voisine du potentiel d'ionisation du monomère.[6] La photolyse de l'isobutène en phase gazeuse à température ordinaire ne donne pas lieu à une polymérisation; en présence de rayonnements ionisants, on obtient des polymères à chaîne très courte.[7]

La polymérisation radiochimique de l'isobutène à $-80°C$ en phase liquide homogène a été interprétée par mécanisme cationique.[8-10] Cette hypothèse a été confirmée par l'étude de la composition de copolymères isobutène–chlorure de vinylidène.[11] On a en effet montré que ce dernier monomère, dont la double liaison est désactivée vis-à-vis de l'attaque d'un cation, ne s'incorpore pas à la chaîne croissante. L'effet accélérateur notable d'additifs solides sur la polymérisation radiochimique de l'isobutène à basse température a été mis en évidence par de nombreux auteurs[8,9,12] et attribué à la capture par le solide des électrons primaires de radiolyse du monomère. Pendant notre travail, une étude détaillée de la polymérisation radiochimique de l'isobutène en présence d'oxyde de zinc a été publiée par Roberts et al.[13] Ces auteurs attribuent l'effet catalytique à une augmentation de la vitesse d'initiation et à une réduction simultanée

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de la vitesse de terminaison, la masse moléculaire étant contrôlée par transfert de chaîne.

Notre travail a mis en évidence l'effet catalytique produit par des additifs de structures chimiques différentes (oxydes, chlorures, sulfates) et de propriétés électriques variées (semi-conducteurs n et p, métaux, graphite, isolants) sur la polymérisation de l'isobutène initiée par les rayonnements γ. Nous avons, de plus, réalisé une étude cinétique de cette polymérisation en présence d'alumine α et synthétisé des copolymères isobutène–chlorure de vinylidène dans les mêmes conditions.

Des essais d'initiation par rayonnement ultraviolet ont également été effectués en présence d'alumine α et d'oxyde de zinc à différentes températures. L'alumine α a été choisie pour l'étude détaillée parce qu'elle présente une structure chimique et cristalline parfaitement définie et est dépourvue, à notre connaissance, de toute activité catalytique en l'absence de radiations, quelle que soit la réaction envisagée.

MÉTHODES EXPERIMENTALES

L'isobutène, de pureté 99,9% (contenant comme impureté principale du 1-butène), a été purifié par passage à travers une colonne de tamis moléculaire 5 Å et distillation sous haut vide (10^{-5} Torr).

Le chlorure de vinylidène a été lavé plusieurs fois au moyen de NaOH 10%, puis à l'eau distillée, séché sur Drierite, et distillé sous pression ordinaire. Le monomère est ensuite séché complètement par distillation à travers une colonne de tamis moléculaire 5 Å et dégazé sous haut vide (10^{-5} Torr).

Les alumines utilisées sont l'alumine U.C.B. pour analyse (I), et des alumines α commerciales Cristalba (II et III). Après calcination à 1350° en présence d'air, leurs surfaces déterminées par la méthode B.E.T. valent respectivement 11,6–0,9 et moins de 0,1 m^2/g. Les oxydes de zinc et de nickel II, III et IV ont été préparés selon la méthode de Stone.[14] L'oxyde de zinc I est l'oxyde de zinc U.C.B. pour analyse. La préparation de l'or colloïdal et du gel d'alumine a été décrite.[15,16] Le naphthalène a été recristiallisé et sublimé sous vide. Le graphite utilisé est nucléairement pur. Les solides ont été dégazés sous haut vide à 400°C, sauf mention spéciale. Les polymérisations ont été effectuées en ampoules scellées remplies et cassées sous haut vide (10^{-5} Torr). Les quantités de monomères mises en jeu ont été mesurées par volumétrie gazeuse (isobutène) et par pesée (chlorure de vinylidène). Le polyisobutène formé a été récupéré par extraction au tétrachlorure de carbone, et les copolymères par extraction à la cyclohexanone. Les masses moléculaires du polyisobutène ont été déterminées par viscosité au moyen de la relation de Fox et Flory.[17] La composition des copolymères a été déterminée par dosage du chlore. Les irradiations γ ont été effectuées au moyen de deux sources de Co^{60} dont les flux valent $2,5 \times 10^5$ et $2,7 \times 10^4$ rad/h. La thermostatisation a été réalisée au moyen du mélange acétone—CO_2 (−78°C) ou de solides à leur

point de fusion: chlorobenzène (−64°C), chloroforme (−45°C), éthylèneglycol (−17°C) et eau (0°C). La dosimétrie a été effectuée par la sulfate ferreux en adoptant 15,5 comme valeur du rendement radiochimique de formation des ions ferriques. Les irradiations ultraviolettes ont été réalisées à l'aide d'une lampe à vapeur de mercure Philips H.P.K. 125 W. L'ampoule à irradier est entourée d'un manchon de quartz dans lequel circule un courant d'azote (préalablement refroidi par de l'air liquide) assurant ainsi une thermostatisation à ± 1°C. Elle est placée le plus près possible de la lampe à vapeur de mercure. L'ensemble est centré dans un réflecteur cylindrique en aluminium poli de 5 cm de diamètre. La dosimétrie a été effectuée sans filtre au moyen d'une solution 0,006*M* de ferrioxalate de potassium selon la méthode de Parker.[18] Cette méthode a permis de déterminer que le rendement global de la lampe pour les longueurs d'onde inférieures à 468 mμ, dans les conditions expérimentales décrites plus haut, est égal à 115.000 rad/h (soit la moitié du rendement de la source au cobalt la plus intense que nous avons utilisée).

RÉSULTATS EXPERIMENTAUX

1. Effets d'Additifs Divers sur la Vitesse de Polymérisation de l'Isobutène

Les résultats obtenus sont groupés dans le Tableau I. On voit que seul le naphthalène, qui se dissout dans le monomère, ne manifeste aucun effet catalytique. Il est remarquable que les oxydes de zinc dopés et non dopés aient une activité catalytique identique. De plus, aucune différence importante n'a été observée entre NiO et ZnO, respectivement semi-conducteurs *p* et *n*.

2. Effet de la Durée et de l'Intensité d'Irradiation, de la Surface d'Additif (α-Al_2O_3) et de la Température sur la Vitesse de Polymérisation de l'Isobutène

L'effet de la durée d'irradiation sur la vitesse de réaction a été étudié à −78°C pour l'alumine I (Fig. 1, Tableau II). La vitesse semble constante jusqu'à un taux de conversion voisin de 60% pour l'alumine I, quel que soit le flux, bien qu'il y ait formation de gel à partir de 10% de conversion environ. La masse moléculaire moyenne diminue entre 6 et 15% de réaction, puis reste constante tant que la vitesse est constante. La vitesse de polymérisation est environ 400 fois plus grande qu'en phase homogène lorsque le milieu réactionnel contient 33% en poids d'alumine I; quant à la masse moléculaire, elle est quatre fois plus élevée (voir Tableau I, 335 et 337). Il faut remarquer que la reproductibilité des résultats est faible, ces derniers pouvant varier de 30% dans des conditions expérimentales apparemment identiques. Le phénomène de non reproductibilité des vitesses de polymérisation radiochimique de l'isobutène en phase homogène ou hétérogène a déjà été signalé par plusieurs auteurs.[10,13]

TABLEAU I

Effet d'Additifs Divers sur la Vitesse de Polymérisation de l'Isobutène et la Masse Moléculaire des Produits Formés[a]

No.	Additif (0,5 g)	S, m²/g	Dose, rad/h $\times 10^{-5}$	Conversion, %	$M_v \times 10^{-3}$	$G \times 10^{-5}$[b]	G_f
379	Na_2CO_3	1,21	1,20	12,3	1.700	0,1760	1,07
159	NaCl		4,64	10,5	671,0	0,0389	0,60
160	Na_2SO_4	<0,1	4,64	10,0	1.110	0,0371	0,34
204	Or colloidal		0,12	24,0	2.415	3,438	14
381	"		"	22,8	2.087	3,261	16
200	Graphite		0,12	14,0	2.636	2,005	7,8
380	"		"	9,92	2.087	1,421	7,0
216	Naphthalène[c]		0,80	0			
222	ZnO III[d]		0,40	49,7	1.615	2,136	13,7
223	ZnO IV[e]		"	38,8	1.407	1,667	12,3
225	ZnO II[e]	1,53	0,80	75,5	861,3	1,622	19,5
217	NiO II[e]	2,9	0,80	25,6	221,2	0,5501	25,7
199	NiO II		"	80,0	566,8	1,7190	31,4
201	Gel d'alumine	187	0,12	80,0 {51,8% polymère, 29,0% dimère}			
211	"		0,06	50,0 {16,7% dimère, 33,4% polymère}			
335	—		17,6	15,8	331,0	0,0154	0,48
337	—		"	18,6	542,4	0,0182	0,35
369[g]	—		20,1	14,0	98,30	0,0120	1,26
378[g]	—		19,3	8,98	97,30	0,0080	0,85

[a] Flux: $2{,}72 \times 10^4$ rad.h^{-1}; température d'irradiation: −78°C; i-C_4H_8 mis en jeu: 1 g.; température de dégazage: 400°C sauf 223, 225, et 217)

[b] Calculé en tenant compte de l'énergie dissipée dans l'isobutène seulement.

[c] Dissous.

[d] Dopé: Li/Zn = 0,05.

[e] Température de dégazage: 200°C.

[f] Dopé: Cr/Zn = 0,02.

[g] Température d'irradiation: 0°C.

[f] Dopé: Cr/Zn = 0,02.
[g] Température d'irradiation: 0°C.

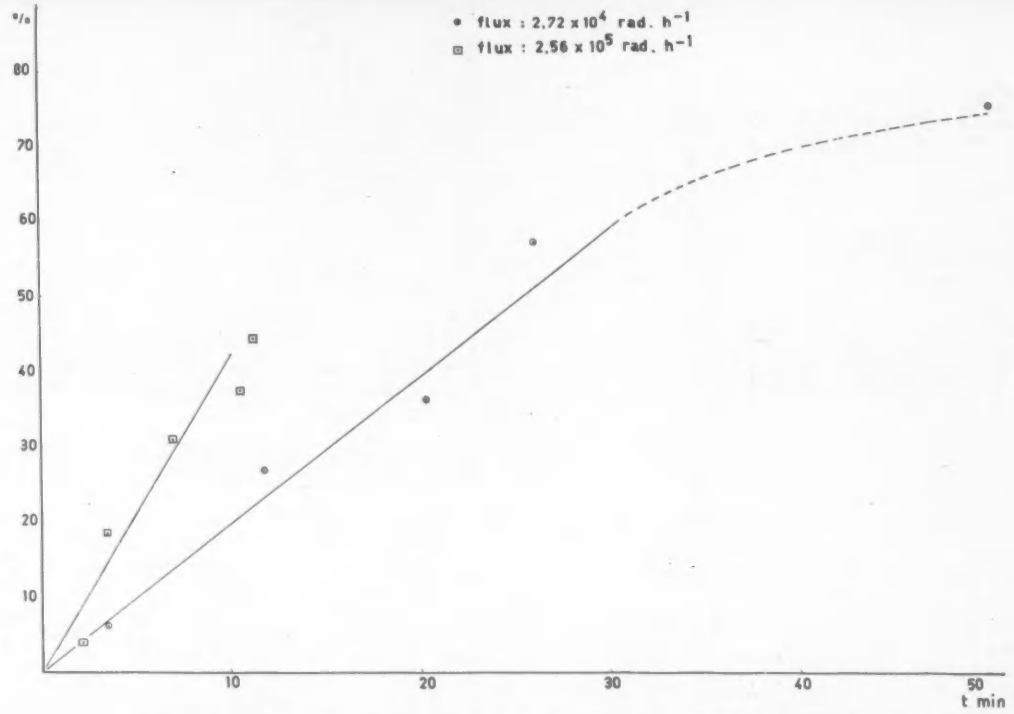

Fig. 1. Effet de la durée d'irradiation et de l'intensité sur la vitesse de polymérisation.

TABLEAU II

Influence de l'Intensité et de la Durée d'Irradiation sur la Vitesse de Polymérisation et la Masse Moléculaire des Produits Formés à −78°C[a]

No.	Flux, rad/h	Dose, rad × 10^{-3}	Conversion, %	$M_v \times 10^{-3}$	$G \times 10^{-4}$[b]	G_i
332	$2,56 \times 10^5$	9,0	3,96	6.461	7,57	1,21
292	"	15,0	18,7	3.085	21,4	7,19
291	"	30,0	31,2	3.294	17,9	5,61
290	"	45,0	37,5	2.007	14,3	7,38
322[c]	"	48,0	44,6	718,7	16,0	23,3
329	2.72×10^4	1,6	6,25	5.244	67,2	13,2
234	"	5,6	11,9	1.503	36,5	23,9
235	"	9,6	36,5	1.174	65,4	57,7
176[d]	"	12,0	57,4	1.718	82,2	49,5
150[e]	"	24,0	75,7	732,0	54,2	76,6

[a] α-Al_2O_3 I mis en jeu 0,5 g; i-C_4H_8 mis en jeu 1,00 g.
[b] Calcul tenant compte de l'énergie absorbée dans l'isobutène seulement.
[c] Moyenne de deux essais.
[d] Moyenne de six essais.
[e] Moyenne de trois essais.

TABLEAU III

Influence de la Température sur la Vitesse de Réaction et la Masse Moléculaire des Produits Formés[a]

No.	T, °C	Flux, rad/h × 10^{-4}	Dose, rad × 10^{-3}	Conversion, %	M_v × 10^{-3}	G × 10^{-5}[b]	G_i
263	−110	2,72	24,0	9,62	3.759	0,689	1,90
202	"	2,83	12,0	4,93			
179	−78	2,88	12,0	57,5	1.699	8,24	50,2
235		"	9,60	36,5			
234		"	5,60	26,9			
329		2,72	1,60	6,25			
220	−64	2,83	6,00	62,3	963,2	17,8	192
317		2,72	3,00	32,0			
318	−45	2,72	1,92	37,5	881,5	33,6	394
328		"	1,42	15,1			
321	−18	2,72	2,88	18,2	196,2	10,9	573
331		"	1,58	7,6			
350		"	2,88	19,7			
265	0	2,72	3,00	10,4			
320		"	6,00	29,9	69,7	8,57	1.272
334	20	2,72	2,63	14,3			
351		"	1,20	6,8	41,4	9,74	2.435
370		"	1,20	7,2			

[a] i-C_4H_8 mis en jeu = 1 g; α-Al_2O_3 mis en jeu = 0,5 g.
[b] Calcul tenant compte de l'énergie dissipée dans l'isobutène seulement.

L'examen des courbes *a* et *b* de la Figure 1 permet d'estimer que la vitesse de polymérisation est proportionnelle à $I^{0,38}$ pour des taux de conversion inférieurs à 30%. Cette valeur sera assimilée à $I^{0,5}$ dans la suite du texte. La masse moléculaire obtenue à haut flux est environ deux fois plus élevée que celle obtenue à bas flux.

L'effet de la température d'irradiation a été étudié entre 20°C et −110°C (Fig. 2 et Tableau III). L'énergie d'activation globale est posi-

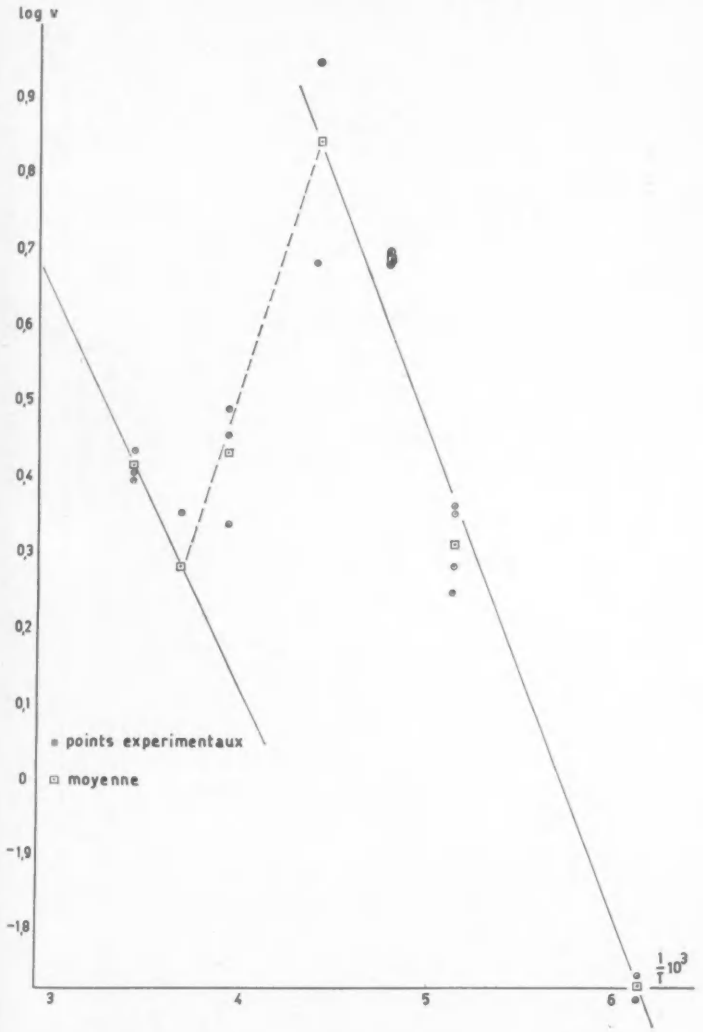

Fig. 2. Effet de la température d'irradiation sur la vitesse de polymérisation.

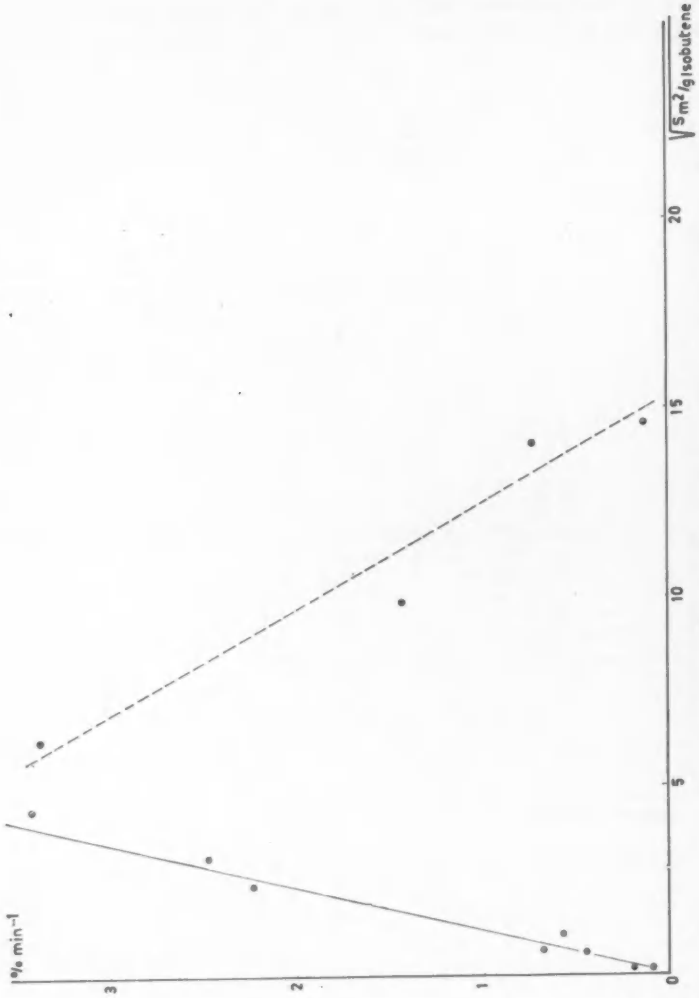

Fig. 3. Effet de la surface d'additif sur la vitesse de polymérisation.

TABLEAU IV

Influence de la Surface d'Additif (α-Al_2O_3) sur la Vitesse de Polymérisation et la Masse Moléculaire des Produits Formés à −78°C

No.	Alumine type et poids, g	i-C_4H_8, g	Flux, rad/h $\times 10^{-4}$	Dose, rad $\times 10^{-3}$	Conversion, %	M_t $\times 10^{-3}$	$G \times 10^{-5a}$	G_j	$G \times 10^{-5b}$	G_t
188	III, 0,5	0,99	2,88	12,0	1,98		0,283			
354	III, 0,5	1,03	2,72	64,0	25,9	4.165	0,695	1,73	0,4633	1,15
187	II, 0,5	0,99	2,88	12,0	16,9	1.851	2,421	13,5	1,614	9,02
343	II, ,05	1,02	2,72	13,1	12,8		1,681			
258	I, 0,1	1,00	2,72	12,0	15,2	1.699	2,176	13,3	1,978	12,1
176[c]	I, 0,5	0,997	2,88	12,0	57,4	"	8,222	50,0	5,481	33,4
257	I, 0,5	0,584	2,72	3,20	17,4	2.112	9,346	45,7	5,731	28,1
256	I, 0,5	0,296	"	3,20	24,2	1.699	12,99	79,2	4,828	29,4
219	I, 1,0	0,297	"	4,00	29,8	938	12,81	14,1	2,865	31,6
363	I, 2,0	0,231	"	4,00	12,6	1.800	5,415	31,1	0,5587	3,21
362	I, 2,0	0,117	"	24,0	37,9	1.727	2,714	16,3	0,1498	0,897
218	I, 2,0	0,109	"	12,0	3,19		0,457		0,0230	
195	I, 10,0	0,113	2,88	44,8	1,38		0,050		0,0006	
194	I, 10,0	0,058	"	12,0	0,42		0,060		0,0003	

[a] Calcul tenant compte de l'énergie dissipée dans l'isobutène seulement.
[b] Calcul tenant compte de l'énergie dissipée dans l'ensemble du système.
[c] Moyenne de six résultats.

tive et égale à 2,8 ± 0,5 Kcal. entre −110°C et −20°C. Vers −45°C on observe une discontinuité à partir de laquelle l'énergie d'activation globale change de signe.

En ce qui concerne l'effet de surface, deux séries d'essais ont été effectuées (Tableau IV). Dans la première série, nous avons fait varier le rapport en poids alumine–monomère; dans la seconde série. Nous avons maintenu constant le rapport en poids alumine–monomère. Nous avons utilisé des alumines de surface spécifique comprise entre 0,1 et 10 m^2/g environ.

Le graphique (Fig. 3) montre que la vitesse de polymérisation est proportionnelle à la racine carrée de la surface d'additif par gramme de monomère lorsque le rapport en poids additif-monomère est inférieur à 3,3 environ (ceci correspondrait à 50 couches monomoléculaires empilées sur la surface d'additif) et décroît ensuite. La masse moléculaire, par contre, reste constante quelle que soit la valeur de la surface si l'on néglige l'essai 354.

3. Préirradiation du Catalyseur

L'alumine I est irradiée en l'absence de monomère à −192°C pendant 50 heures sous un flux de $2,2 \times 10^5$ rad/h. Le monomère est ensuite mis en contact avec le solide maintenu à −192°C. L'ensemble est ensoite réchauffé jusqu'à −78°C. Le taux de conversion obtenu est 0,5% après trois jours.

4. Étude de la Composition de Copolymeres Formés en Présence d'Alumine α

On a étudié la composition des copolymères isobutène-chlorure de vinylidène obtenus entre −78°C et 0°C par irradiation γ en présence d'alumine

TABLEAU V

Copolymérisation Isobutène (M_1)–Chlorure de Vinylidène (M_2)

No.	$\left(\frac{M_1}{M_1 + M_2}\right)_{t=0}$	$\left(\frac{M_1}{M_1 + M_2}\right)_{pol.}$	T, °C
	A. Sans additif, initiation par U.V.		
372	0,50	0,28	0
	B. Sans additif, initiation par γ		
231	0,50	b,99	−78
—[a]	0,50	0,96	"
—[a]	0,50	0,64	−45
—[a]	0,50	0,33	0
	C. Avec additif,[b] initiation par γ		
228	0,50	>0,99	−78
293	0,50	>0,99	−45
376	0,50	0,98	−20
373	0,50	I → 0,48[c]	0
		II → 0,99	

[a] Voir Sheĭnker, et al.[11]

[b] 0,5 g α-Al_2O_3I pour 1 g de monomère.

[c] Le polymère a été séparé en deux fractions: I correspond à 28,5% en poids, II correspond à 71,5% en poids.

(Tableau V). Ces résultats sont comparés à ceux obtenus par Sheinker[11] pour la même composition initiale en l'absence de solide. On voit que le chlorure de vinylidène ne s'incorpore pas à la chaîne croissante pour des températures inférieures à 0°C en présence de solide, alors qu'en l'absence d'additif, le copolymère formé à −45°C contient 33% de chlorure de vinylidène. A 0°C en phase hétérogène, on obtient un mélange de polyisobutène et de copolymère.

Les copolymères formés à la même température en phase homogène sous irradiation ultraviolet et γ ont des compositions très voisines, $M_1/(M_1 + M_2)$ valant respectivement 0,28 et 0,33.

5. Irradiation par Rayons Ultra-violets

Des mélanges α-Al_2O_3–isobutène et ZnO–isobutène ont été irradiés au moyen d'une lampe à vapeur de mercure à 0°C et −78°C (Tableau VI). Les rendements en polymère obtenus sont trop faibles pour que les viscosités puissent être mesurées avec grande précision. Les résultats particulièrement douteux sont signalés entre parenthèses.

TABLEAU VI

Initiation de la Polymérisation de l'Isobutène au Moyen de Rayonnement Ultra-violet[a]

No.	Additif	Durée d'irradiation, h:min	T, °C	Conversion (polymère + dimère), %	Dimère formé, %	M_v
238	ZnO (U.C.B.)	20:35	0	5,1	3	(32.600)
246	"	34:45	"	5,5	3,4	(70.315)
277	"	—	"	0,67	—[b]	
264	α-Al_2O_3 I	34:45	"	5,0	3	9.790
260	"	—	"	0,21	—[b]	
278	—	35:20	"	0,21	—[b]	
312	ZnO (U.C.B.)	16:50	−78	0,40	Traces	458.000
338	"	35:10	"	0,40	"	
323	"	32:40[c]	"	0,03	—[b]	
324	"	32:00[d]	"	0,04	—[b]	
275	α-Al_2O_3 I	36:25	"	1,22	Traces	650.000
342	"	33:45	"	0,3	—[b]	

[a] Additif mis en jeu: 0,5 g; i-C_4H_8 mis en jeu: 1 g.
[b] Quantité non détectable après condensation dans un piège.
[c] Filtre absorbant $\lambda < 4.000$ Å.
[d] Filtre absorbant $\lambda < 3.000$ Å.

Les résultats obtenus montrent qu'à 0°C il existe un mécanisme d'interaction spécifique important entre le solide et le monomère, mais cette interaction conduit essentiellement à la formation de dimère qui est inhibiteur de la polymérisation. L'essai 176 (Tableau II) donne 57,4% de conversion. Une ampoule identique, irradiée pendant 12 h. à 0°C par des rayons ultraviolets puis irradiée à −78°C dans les mêmes conditions que

176 donne seulement 0,2% de conversion. A −78°C, une faible quantité de polymère se forme lorsque les longueurs d'ondes utilisées sont inférieures à 3.000 Å. Aucune différence significative n'est observée entre l'alumine et l'oxyde de zinc, malgré la différence entre les spectres d'absorption de ces deux solides dans l'ultra-violet.[19,20] L'isobutène n'absorbe pas dans le domaine de longueurs d'onde émis par la vapeur de mercure (si ce n'est peut-être faiblement à 1840 cm^{-1}. Cette absorption sera d'ailleurs encore atténuée par la faible transparence du quartz à cette longueur d'onde.).

DISCUSSION

La cinétique de polymérisation radiochimique de l'isobutène en phase liquide a été étudiée par Charlesby et ses collaborateurs.[8] Les caractéristiques en sont les suivantes: vitesse indépendante de I, énergie d'activation globale négative, taux de conversion tendant vers une limite apparente de 30% et absence de transfert de chaîne. Le schéma cinétique proposé et les vitesses de reaction sont:

Initiation:	$(CH_3)_2C{=}CH_2 \rightsquigarrow X^+ + \epsilon$	$R_i I$
	$X^+ + M \rightarrow XM^+$	
Propagation:	$XM_n^+ + M \rightarrow XM_{n+1}^+$	$k_p[XM_n^+][M]$
Formation d'inhibiteur:	$M \rightsquigarrow A$	$R_a I$
Terminaison monomoléculaire:	$XM_n^+ + \epsilon \rightarrow P_n$	$k_t[XM_n^+]$
Terminaison par inhibiteur:	$XM_n^+ + A \rightarrow P_n + A^+$	$k_a[XM_n^+][A]$

On obtient ainsi:

$$-dM/dt = k_p\,[XM_n^+][M] = k_p[M]R_i I/k_t + k_a R_a I t$$

Dans le cas de la polymérisation en phase hétérogène, à −78°C, la vitesse est proportionnelle à $\sqrt{S_{m^2/g\ \text{isobutène}}}$ (pour les valeurs de ce paramètre inférieures à 5) et à $I^{0,5}$. Le taux de conversion n'est pas limité à 30%.

Ces résultats peuvent être interprétés si l'on suppose que l'initiation a lieu sur la monocouche adsorbée à la surface du solide, cette dernière retenant l'électron éjecté par la molécule d'isobutène, et que la terminaison est bimoléculaire. Une interaction importante entre solide et monomère doit également intervenir lors de la polymérisation initiée par les rayons ultraviolets (Tableau VI) puisque l'énergie maximum des photons émis par la lampe est inférieure au potentiel d'ionisation de l'isobutène.

On peut alors écrire:

Initiation:	$(CH_3)_2C{=}CH_2 \rightsquigarrow X^+ + \epsilon\,(S)$		$R_i IS$
Terminaison:	$XM_n^+ + \epsilon\,(S) \rightarrow P_n$		$k_t[XM_n^+][\epsilon(S)]$
		ou	$k_t[XM_n^+]^2$

La propagation de chaîne a lieu en phase homogène et non à la surface du solide puisque la vitesse est fonction de la surface par gramme de monomère et pas seulement de la surface. On obtient ainsi:

$$-dM/dt = k_p[\mathrm{M}](v_i/k_t)^{0,5}$$

De nombreux mécanismes ont été envisagés pour justifier que la fonction $v = f(S^{0,5})$ passe par un maximum, mais aucun n'a été satisfaisant. On pourrait cependant admettre que la chute de vitesse observée serait due à une diminution de la quantité de monomère accessible à la chaîne croissante.

La nature de l'interaction entre l'additif et le monomère et entre l'additif et l'électron est difficile à préciser puisque des substances de structures aussi différentes que des semi-conducteurs n et p, des isolants, l'or et le graphite manifestent des propriétés catalytiques très voisines. Il ne s'agit cependant pas d'une modification durable du catalyseur par irradiation puisque la polymérisation n'a pas lieu sur le catalyseur préirradié à la température de l'azote liquide.

Les valeurs de $G_{\text{initiation}}$ obtenues au moyen de l'équation $G_i = G/\overline{\mathrm{DP}}$ (Tableaux II, III et IV) sont supérieures à $100/\Delta H$ où ΔH est l'enthalpie d'initiation[2] et vaut 8,5 eV pour l'ionisation de l'isobutène et 3,9 eV pour l'arrachement d'un radical H au monomère. La masse moléculaire est donc essentiellement contrôlée par transfert de chaîne, la vitesse de transfert augmentant plus vite que la vitesse de propagation avec la température. Ceci est, de plus, confirmé par le fait que la masse moléculaire dépend peu de I et est indépendante de S dans les conditions étudiées.

Le coefficient de température global, positif pour la polymérisation en phase hétérogène entre $-110°C$ et $-45°C$ et négatif pour la polymérisation homogène, confirme l'existence d'une différence de mécanisme entre ces deux réactions. La réaction reste cependant ionique entre $-110°C$ et $-20°C$, ainsi que le suggère la composition des copolymères obtenus en présence d'alumine α. En ce qui concerne les résultats obtenus à température plus élevée, les discontinuités observées entre $-45°C$ et $-20°C$ pour la vitesse de réaction, et entre $-20°C$ et $0°C$ pour la composition des copolymères suggèrent qu'il y aurait changement de mécanisme dans ce domaine de température. A $0°C$, on aurait deux mécanismes concurrents, l'un ionique et l'autre radicalaire. Il faut remarquer que la vitesse de polymérisation à $0°C$ est également fortement accélérée en présence d'alumine tandis que la masse moléculaire ne change pas (Tableau I, 369 et 378).

CONCLUSION

L'effet de radiocatalyse observé à $-78°C$ pour la polymérisation de l'isobutène en présence d'additifs est, au moins en partie, dû à un changement de mécanisme.

L'étude de la composition de copolymères obtenus en phase hétérogine et du coefficient de température global de la réaction de polymérisation

montre qu'il y a passage d'un mécanisme ionique à un mécanisme radicalaire entre −20°C et 0°C.

La polymérisation en phase hétérogène semble pouvoir être initiée par rayonnement ultra-violet.

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Résumé

Plusieurs travaux récents ont montré d'une part, que la polymérisation de l'isobutène initiée par rayonnement γ en phase liquide homogène à −80°C obéit à un mécanisme cationique et, d'autre part, que cette réaction est fortement accélérée en présence de solides ioniques finement divisés. Au cours de notre travail, un grand nombre d'autres solides ont été testés parmi lesquels des semi-conducteurs *n* et *p*, des isolants tel α-Al_2O_3, l'or colloidal et le graphite. L'effet catalytique observé est général, quelles que soient les propriétés électriques ou la structure chimique des dérivés utilisés. Une étude détaillée a été réalisée en présence d'alumine α. La vitesse globale de polymérisation

augmente avec la température entre −110°C et 0°C lorsque la réaction est effectuée en présence d'additif, tandis qu'elle diminue avec la température pour la même réaction en phase homogene. La masse moléculaire obtenue en milieu hétérogène est fonction décroissante de la température. L'étude de la composition de copolymères isobutène–chlorure de vinylidène formés à −80°C confirme néanmoins l'existence d'un mécanisme cationique. L'effet de la durée d'irradiation, de l'intensité du rayonnement γ, de la surface spécifique et du volume de l'additif ainsi que la possibilité de transfert de chaîne ont également été étudiés. Nous avons de plus utilisé comme initiateur le rayonnement ultraviolet émis par une lampe à vapeur de mercure pour la polymérisation de l'isobutène en présence d'oxyde de zinc, en présence d'alumine et en phase homogène. Un mécanisme est proposé en fonction des données cinétiques.

Synopsis

Several recent works have shown that the polymerization of isobutene initiated by gamma-rays in liquid homogenous medium at −80°C. proceeds through a cationic mechanism; moreover, the reaction is strongly accelerated by the presence of finely dispersed ionic solids. In the present work, several solids have been tested, as e.g., semi-conductors *n* and *p*, isolators as α-Al_2O_3, colloidal gold, and graphite. The catalytic effect is generally observed, whatever may be the electrical properties on the chemical structure of the substances. A detailed study has been carried out with α-Al_2O_3. The overall rate of polymerization increases with the temperature between −110°C. and 0°C. when the reaction is carried out in the presence of additive, while it diminishes with the temperature for the same reaction in homogeneous phase. The molecular weight of the sample obtained in heterogeneous system decreases with the temperature. The study of the composition of isobutene–vinylidene chloride copolymers prepared at −80°C. confirms, nevertheless, the existence of a cationic mechanism. The effects of the duration of irradiation of the gamma-radiation intensity, of the specific surface and of the volume of the additive have been considered, as well as the chain transfer possibility. We have also used as initiator a ultraviolet mercury band for the polymerization of isobutene at 0°C. in homogenous system, and in the presence of zinc oxide, and of aluminoxide. A mechanism is proposed in function of these kinetic data and of the electronic excitation spectrum of the solids.

Zusammenfassung

Mehrere neuere Arbeiten haben einerseits gezeigt, dass die γ-Strahlen-gestartete Polymerisation von Isobuten in homogener flüssiger Phase bei −80°C nach einem kationischen Mechanismus verläuft und andrerseits, dass diese Reaktion in Gegenwart feinverteilter Ionenfestkörper stark beschleunigt wird. Bei unseren Versuchen wurde eine gross Zahl anderer Festkörper, darunter *n*- und *p*-Halbleiter, Isolatoren wie α-Al_2O_3, kolloides Gold, und Graphit, geprüft. Unabhängig von den elektrischen Eigenschaften und der chemischen Struktur der verwendeten Derivate wurde eine allgemeine katalytische Wirksamkeit beobachtet. Eine eingehende Untersuchung wurde mit α-Tonerde durchgeführt. Bei Gegenwart des Zusatzmittels nimmt die Bruttogeschwindigkeit der Polymerisation zwischen −110°C und 0°C zu, während sie bei der gleichen Reaktion in homogener Phase mit der Temperatur abnimmt. Das in heterogenem Milieu erzaltene Molekulargewicht bildet eine abnehmende Funktion der Temperatur. Die Untersuchung der Zusammensetzung der bei −80°C gebildeten Isobuten-Vinylidenchlorid-Copolymeren bestätigt nichtsdestoweniger das Vorliegen eines kationischen Mechanismus. Weiters wurde der Einfluss der Bestrahlungsdauer, der Intensität der γ-Strahlung, der spezifischen Oberfläche und des Volumens des Zusatzes sowie die Möglichkeit einer Kettenübertragung untersucht. Schliesslich wurde zum Start der Polymerisation von Isobuten in Gegenwart von Zinkoxyd, von Aluminiumoxyd und in homogener Phase noch die Ultravioletttstrahlung einer Quecksilberdampflampe verwendet. Auf Grund der kinetischen Ergebnisse wird ein Reaktionsmechanismus aufgentellt.

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Radiation-Induced Polymerization at High Pressures*

LEO A. WALL and DANIEL W. BROWN, *National Bureau of Standards, Washington, D. C.*

INTRODUCTION

Radiation from cobalt-60 is capable of initiating the polymerization of many substances. For the study of polymerization at high pressures and various temperatures it has many practical and theoretical advantages. Relatively simple apparatus may be used since no special windows for the radiation are needed, as would be necessary if one were to carry out high pressure polymerization using ultraviolet light. *A priori* one anticipates that the rate of initiation will be essentially independent of pressure as well as temperature.

For most elementary reactions of the bimolecular type there is a net decrease in volume upon the formation of the transition complex. On this basis reaction rates increase with the application of pressure. In polymerization systems there are usually competing reactions, propagation, transfer, and often other side reactions. The first favors high polymer production, while the latter two favor low molecular weight products. High pressure investigation of polymerization is a feasible method for determining which of the competing reactions are most influenced by pressure and hence which have the greater volume decreases in the transition complex.

In this work several monomers that are normally not polymerized by free radicals were studied. The most intensively investigated monomers were propylene, perfluoroheptene-1, and carbon disulfide. Other monomers studied were trifluorovinyl phenyl ether, trifluorovinyl pentafluorophenyl ether, and 4-chloroperfluoroheptadiene-1,6. Some preliminary results indicate that carbon monoxide and carbon dioxide can be copolymerized with tetrafluoroethylene.

EXPERIMENTAL

The polymerization procedure consisted of filling an appropriate pressure vessel with monomer, usually degassed, and exposing the vessel to radiation from a Co^{60} source. Two Co^{60} sources were used, one of 1200 curies which can be used to give the sample in the pressure vessel a maximum average

* Based on research supported by the U. S. Army Research Office, Durham, North Carolina.

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dose rate of 0.13 Mrad/hr., and one of 50,000 curies capable of giving the sample a dose rate of 3 Mrad/hr.

The pressure vessels are simple cylinders, made of hardened steel or beryllium copper, in which pressure is applied to about 17 cc. of sample by means of a piston pushed by a hydraulic ram. A threaded cap follows the piston and holds it in the vessel so that the vessel can be removed from the press and irradiated without losing pressure. While in the press, the vessel is brought to the desired temperature, which is maintained constant within 1°C. by a proportionating controller. The pressure is then adjusted before removal of the vessel from the press. The pressure in the vessel is calculated from the oil pressure in the hydraulic system of the press. Approximate corrections are applied for piston friction and cap distortion. The vessels can be used continuously for experiments at pressures of 10,000–15,000 atm. At higher pressures their useful life is shortened.

The most critical part of the pressure system is the seal which prevents the contents of the vessel from leaking past the piston. A Bridgman-type seal[1] was used. The materials and design of the seal were modified in order to minimize the friction between the cylinder wall and the piston.

RESULTS

The rates of polymerization were determined by dividing the conversion by time. The conversions were relatively low in the range 0–20%. Low molecular weights were determined with a vapor pressure osmometer or by means of viscosity measurements. Intrinsic viscosities of the high molecular weight polymers were usually obtained if the polymers were soluble.

The polymers produced had maximum degrees of polymerization around 75. At low radiation intensities rates of polymerization at constant pressure for both monomers varied linearly with the square root of the intensity. However, at intensities above 0.01 Mrad/hr. the rates of polymerization dropped off. This effect appears to be explainable by the premise[2] that the rate of initiation is large enough to result in termination of many of the growing radicals by primary radicals.

The degree of polymerization of polypropylene from experiments at 14,600 atm. and 21°C. was essentially independent of the rate of polymerization. The inherent viscosities of many of the polypropylene samples were measured in decalin at 135°C. The viscosity-average degree of polymerization, DP_V, was calculated by using the relation of Chiang.[3] The maximum inherent viscosity of our samples was 0.11, whereas the minimum value in his calibration is 1.5. Qualitatively the changes in DP_V with reaction conditions parallel those in DP_n, but the calculated $\overline{DP}_V$ is as much as four times $\overline{DP}_n$. This ratio is not firmly fixed owing to the uncertainty of the extrapolation.

Infrared spectra of the polypropylenes are more like those of molten Ziegler-Natta polymers than the products of the low-temperature acid-

catalyzed polymerization.[4] There is evidence that propyl and vinyl groups are present in small amounts. This presumably reflects the relatively low molecular weight of our polymers. Terminal ethyl groups do not seem to be present.

The polypropylenes range from faintly colored materials similar to the low molecular weight polyisobutylene oils to opalescent gums so viscous that they retain impressions for several days. The latter gums have the higher molecular weights. All the polypropylenes are soluble in benzene at room temperature. Sometimes the solutions are opalescent, but they pass through coarse frits without loss of polymer or opalescence.

At a constant pressure of 17,100 atm. and 139°C. the reciprocal degree of polymerization versus rate of polymerization behavior of the polyperfluoroheptene allowed one to estimate a transfer constant of 0.023 to 0.032 and a $G(i)$, radicals per 100 e.v. of absorbed energy, of 16 to 7 assuming disproportionation. Assuming the G value for initiation to be independent of pressure, one can estimate the other transfer constants from one or two experiments at different pressures. Experimental results are shown in Table I.

Trifluorovinyl pentafluorophenyl ether and 1,1,2-trifluorovinyl phenyl ether have been prepared in our laboratories and have not been polymerized by the normal free-radical methods. At 12,000 atm., 100°C., and 0.0032

TABLE I

n-Tetradecafluoroheptene-1 Rates and Polymer Characterization[a]

Pressure, atm. × 10^{-3}	Temp., °C.	$10^6 R_p$, hr.$^{-1}$	DP_n	(k_3/k_2)
8.1	97	23.5		
8.1	125	54.5		
8.1	146	73.9		
8.1	168	40.9		
11.9	93	88		
11.9	140	378	42 ± 2	negative to 0.005[b]
11.9	166	521		
11.9	183	486		
11.9	237	2.5		
17.1	94	109	19 ± 1	
17.1	139	1047	26 ± 1	0.023–0.032
17.1	189	3760	76 ± 8[c]	
17.1	211	6113	52 ± 2	0.016–0.018[b]
17.1	267	7240	17 ± 1	
17.1[d]	140	2.9		
17.1[d]	214	241	30 ± 1	

[a] Dose rate = 0.0027 Mrad/hr. unless specified.

[b] Low value assumes $G(i) = 16$ with disproportionation; high value assumes $G(i) = 7$ with disproportionation.

[c] Polymer subjected to prolonged evacuation before measuring DP_n.

[d] Thermal polymerization.

Mrad/hr. the trifluorovinyl pentafluorophenyl ether gave 2.7% conversion to polymer. The $G(M)$, G value for monomer consumption, was 283. Similar experiments on 1,1,2-trifluorovinyl phenyl ether are summarized in Table II. Large $G(M)$ values were attained; however, the intrinsic viscosities indicate relatively low molecular weights.

TABLE II
Polymerization of 1,1,2-Trifluorovinyl Phenyl Ether

Pressure, atm. $\times 10^{-3}$	Temp., °C.	Dose rate, Mrad/hr.	10^6R_p, hr.$^{-1}$	$G(M)$, molecules/ 100 e.v.	$[\eta]$, dl./g.
6.4	102	1.06	2810	14	0.03
10.0	191	0.0027	—[b]	0	—
14.0	145	0.0027	236	455	0.026
~14.0[a]	103	0.0027	687	1190	0.03

[a] Monomer freezes at 6,400 atm. at this temperature. Pressure may not have been uniform.

[b] Very high yield of material tentatively identified as dimer.

TABLE III
Polymerization of 4-Chloroperfluoroheptadiene-1,6

Pressure, atm.	Temp., °C.	Time, hr.	Dose rate, Mrad/hr.	Conversion, %	$[\eta]$, dl./g.
~1	150	71	0.2	100	0.09
~1	100	71	0.2	60	0.05
<1	30	504	0.2	45	0.04
~1	160	336	U.V.	50	0.04
1.36×10^3	147	113	0.003	100	0.60

Another fluorocarbon monomer studied was 4-chloroperfluoroheptadiene-1,6. Results of the study are shown in Table III. Polymerization of the degassed monomer in sealed evacuated tubes gave a product of low molecular weight, as indicated by the low intrinsic viscosity. These materials are clear brittle solids of poor physical properties. The material produced under high pressure with $[\eta] = 0.60$ dl./g. is, on the other hand, a tough flexible material.

Carbon disulfide has been polymerized previously[1,5] by heating the liquid to temperatures of 185°C. or greater at pressures of the order of 55,000 atm. to give a black solid; its infrared spectrum[5] suggests that a good portion of material has the structure

Table IV summarizes our results. It is believed that gamma radiation facilitates this polymerization. The material formed at 1 atm. is a tan

TABLE IV
Polymerization of Carbon Disulfide

Pressure, atm. $\times 10^{-3}$	Dose, Mr[a]	Temp., °C.	Yield, %	$G(M)$
0.001	211	62	0.95	0.65
4	221	66	0.86	0.60
10	400	98	4.1	1.5
10	153	100	1.46	1.4
14	149	66	1.3	1.3
15	18	20	0.15	1.0[a]

[a] Dose rate 0.13 Mrad/hr.; all other 3.2 Mrad/hr.

color and is believed to be mainly decomposed carbon disulfide. The material produced at high pressure is definitely a deep black. The $G(M)$ values are low, but show a definite increase with temperature and pressure. The polymer is not soluble in monomer though it appears to be highly swollen with its monomer. Upon thermal decomposition in a vacuum system, about 30% of the polymer is converted back to liquid carbon disulfide. The rest of the polymer is converted to complex sulfur-carbon compounds and an apparently carbon residue.

DISCUSSION

Polypropylene

The results on the polymerization of propylene are readily interpreted within the framework of accepted free-radical polymerization mechanisms. Since the DP is independent of the rate of polymerization at a given pressure and temperature, we assume that $DP_n = k_2/k_3$, the ratio of the propagation constant to the monomer transfer constant. The variation of DP_n and rate of polymerization with pressure is given in Figure 1. Since the DP increases with pressure rather less than the rate, it is evident that both the propagation and the monomer transfer constant are increasing with pressure. Plotting the log of the rates and DP versus reciprocal temperature at a given pressure, on the basis of transition state theory for abolute rates, allows one to estimate the enthalpy differences for the reactants going to the activated states. Taking our gamma-ray initiated rates of polymerization to be given by:

$$-dM/Mdt = (k_i/2k_4V)^{1/2}k_2$$

where k_i, the fractional rate of initiation, equals $G(i)Im/N100$, N being Avogadro's number, m the molecular weight of the monomer, I the radiation intensity in electron volts of absorbed energy per gram per second, $G(i)$ the yield of initiating radicals per 100 e.v. of absorbed energy, and V the molar volume of monomer. If $G(i)$ is taken to be independent of temperature, the rate constants for propagation, k_2, and termination, k_4, are the only quantities dependent on temperature. From the temperature dependence

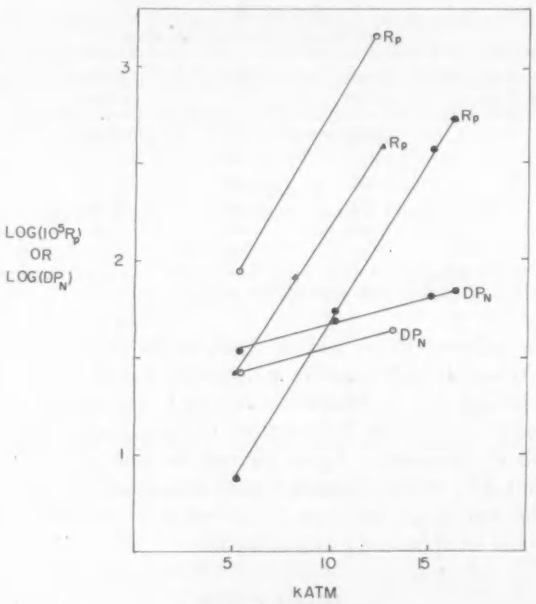

Fig. 1. Polymerization of propylene. Variation of rate of polymerization R_p and number-average degree of polymerization with pressure at a radiation dose rate of 0.0031 Mrad/hr.: (○) 83°C.; (△) 48°C.; (●) 21°C.

of the rate, we can then estimate $\Delta H_2^* - (\Delta H_4^*/2)$. Knowing the dose rate I and assuming $G(i)$ to be 1, $\Delta S_2^* - (\Delta S_4^*/2)$ can be estimated. $G(i)$ is also assumed to be independent of pressure. Taking $G(i)$ as 10 would not change the estimates greatly; measured $G(i)$'s for unsaturated hydro-

TABLE V
Thermodynamic Quantities in Rate of Polymerization Expressions for Propylene

Pressure, K atm.	Form of sum[a]	ΔF^*, cal./mole	ΔH^*, cal./mole	ΔS^*, cal./mole-°C.
5.0	$\Delta_2^* - (\Delta_4^*/2)$	15,860	7,800	−27.3[b]
12.0	$\Delta_2^* - (\Delta_4^*/2)$	14,450	8,160	−21.4[b]
16.4	$\Delta_2^* - (\Delta_4^*/2)$	13,270	8,400[c]	−16.6[b]
5.0	$\Delta_2^* - \Delta_3^*$	−2,070	−855	4.13
12.0	$\Delta_2^* - \Delta_3^*$	−2,330	−760	5.34
16.4	$\Delta_2^* - \Delta_3^*$	−2,500	−700[c]	6.12

[a] Each thermodynamic function to the right is made up of elements having the form defined in this column.

[b] Assumed that $G(R) = 1$.

[c] By extrapolation of values at 5 and 12 K atm.

carbons are normally in this range of values. Table V contains the estimated values of the thermodynamic quantities. From the DP data, estimates of $\Delta H_2^* - \Delta H_3^*$ and $\Delta S_2^* - \Delta S_3^*$ were also made and are presented in Table V.

The variation of log DP_n with pressure P at constant temperature for our system is:

$$\log DP_n = \frac{(-\Delta V_2^* + \Delta V_3^*)P}{2.3RT} + C_1$$

Also

$$\log R_p = \left[\frac{-\Delta V_2^* + (\Delta V_4^*/2)}{2.3RT}\right] P + C_2$$

Here C_1 and C_2 are integration constants. The slopes in Figure 1, therefore, may be used to calculate the sums of the ΔV^*'s. The sum $(\Delta V_2^* - \Delta V_3^*)$ is -1.57 cc./mole at 21°C. and -1.67 cc./mole at 83°C. The sum $(\Delta V_2^* - \Delta V_4^*/2)$ in cc./mole is: -9.62 at 21°C., -9.64 at 48°C., and -12.12 at 83°C.

Perfluoroheptene-1

The radiation-induced polymerization of perfluoroheptene at various pressures between 8,000 and 17,000 atm. is also best treated within the framework of a free-radical mechanism. However, it seems that at the highest temperatures studied a back reaction occurs, as can be seen by the three upper full-line curves in Figure 2, which is a plot of log $R_p - 0.5$ log T versus the reciprocal of the absolute temperature. The 0.5 log T results from the temperature dependence of the preexponential terms in the absolute rate as applied in this case using the usual free-radical mechanism for polymerization. By introducing a depropagation step in the free-radical polymerization mechanism, the rate expression becomes

$$-dM/Mdt = (k_i/2k_4V)^{1/2}\,(k_2 - k_{-2}M^{-1})$$

If no back reaction occurs, the log plots in Figure 2 should follow the dotted extension of the straight portions of the full lines. The difference in rate between the dotted lines and the full lines is assumed to be the rate of back reaction or depolymerization. At the intersection of the dotted and dashed lines the rate of polymerization equals the rate of depolymerization. The temperature at these intersections is then by definition the ceiling temperature. From the data in Figure 2 one estimates the thermodynamic quantities in the absolute rate expressions. These are given in Table VI. They do not depend strongly on the value assumed for $G(i)$. From the DP_n measurements at 17,100 atm. and 139°C., $G(i)$ was estimated to be in the range 7–16 if termination was by disproportionation of radicals, or 14–32 if termination was by combination of radicals. For the purpose of calculating the values presented in Table VI, $G(i)$ was taken to be 25.

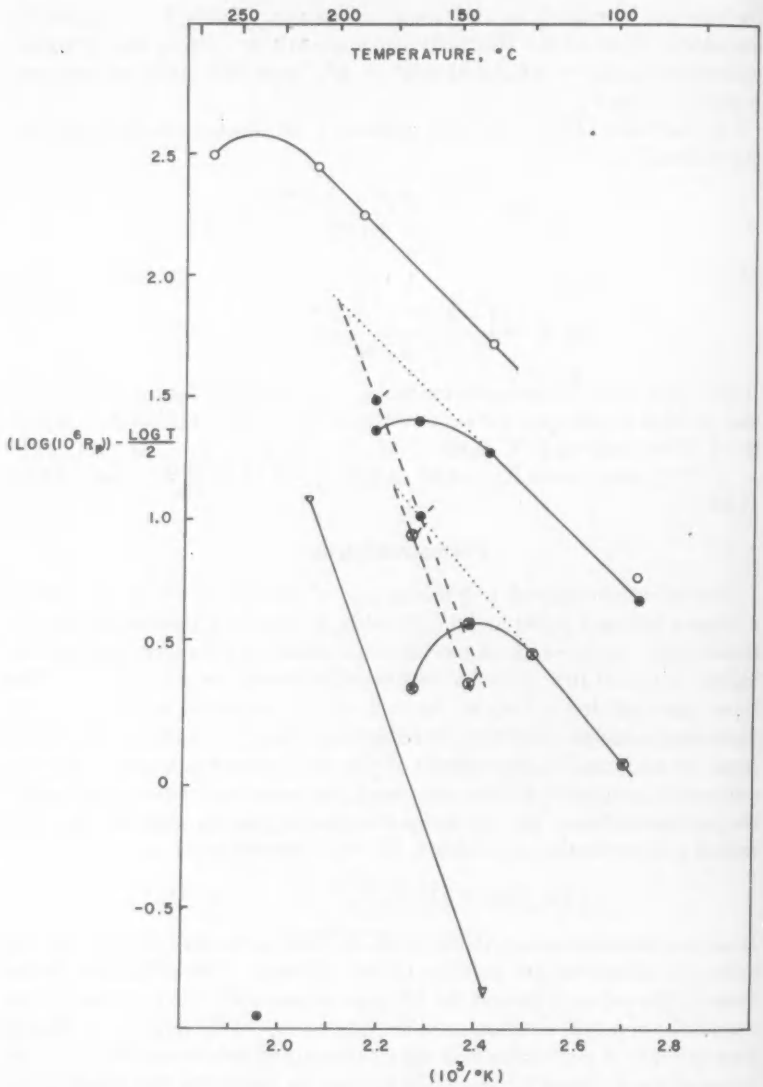

Fig. 2. Polymerization of *n*-Perfluoroheptene-1. Variation of rate of polymerization with temperature: (○) 17,100 atm., dose rate 0.0027 Mrad/hr.; (●) 11,900 atm., dose rate 0.0027 Mrad/hr.; (⊗) 8,100 atm., dose rate 0.0027 Mrad/hr.; (▽) 17,100 atm., thermal polymerization. Full lines (—) indicate polymerization; dashed lines (- -) indicate depolymerization; points with primes are for the depolymerization reaction; intersection of dotted and dashed lines gives the ceiling temperature.

The plot of log R_p versus pressure was curved. This indicates a changing value of $\Delta V_2^* - 0.5\Delta V_4^*$ with pressure. This volume term for polymerization at 139°C. was estimated to be <-13.6 cc./mole at 8,100 atm., -9.4 cc./mole at 11,900 atm., and >-6.8 cc./mole at 17,100 atm.

TABLE VI
Thermodynamic Quantities in Rate of Polymerization Expressions for Perfluoroheptene-1[a]

Pressure, Reaction atm. × 10^{-3}	Temp., °C.	ΔF^* cal./mole	ΔH^*, cal./mole	ΔS^*, cal./mole-°C.
Polymerization				
8.1	139	18640	10500	−19.8
11.9	139	17500	9070	−20.5
17.1	139	16630	9560	−17.1
17.1	189	17500	9560	−17.2
Depolymerization				
8.1	139	19500	21900	5.8
11.9	139	19230	21500	5.5

[a] Each thermodynamic quantity is made up of elements having the form $\Delta_2^* - 0.5\Delta_4^*$.

Since we have in Table VI the differences of the thermodynamic quantities between the reactants and the transition complex for both polymerization and depolymerization of perfluoroheptene-1 at two pressures, we can,

TABLE VII
Thermodynamics of Polymerization at 139°C. for Perfluoroheptene^{-1}

Pressure, atm. × 10^{-3}	ΔF, cal./mole	ΔH, cal./mole	ΔS, cal./mole-°C.	T_c, °C.[a]
8.1	−760	−11400	−25.6	172
11.9	−1730	−12430	−26.0	205

[a] T_c in °K. $= (\Delta H/\Delta S)$.

by taking the differences of these quantities, obtain the free energy, entropy, and enthalpy for the overall polymerization process at each of the two pressures. These data and the ceiling temperatures at the two pressures are given in Table VII.

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Synopsis

Several radiation-induced polymerizations reactions were investigated at pressures between 5,000 and 17,000 atmospheres and temperatures between 20 and 275°C. The most detailed studies have been with propylene and *n*-tetradecafluoroheptene-1. With both monomers the variation of rate of polymerization, R_p, with temperature and radiation intensity is consistent with a free radical mechanism. The maximum number of monomer units converted to polymer per 100 e. v. absorbed, $G(M)$, is 108,000 and 7,600 in the polymerization of propylene and the heptene, respectively; thus, the kinetic chains are long. However, the number-average degree of polymerization, DP_n, is low, the maximum values being about 75 in both polymerizations. In the polymerization of propylene, transfer to monomer limits DP_n; the transfer constant becomes greater as temperature increases or pressure decreases. In the polymerization of the heptene, DP_n is determined by both transfer and termination. In the latter polymerization both R_p and DP_n first increase and then decrease as the temperature is raised at constant pressure because the depolymerization rate becomes appreciable at high temperature and reduces the observed R_p.

Résumé

De nombreuses réactions de polymérisation induites par les radiations ont été étudiées à des pressions comprises entre 5.000 et 17.000 atmosphères et à des températures comprises entre 20°C et 275°C. Les études les plus détaillées ont été effectuées sur le propylène et le *n*-tétradécafluoroheptène-1. Pour ces deux monomères, la variation de la vitesse de polymérisation R_p en fonction de la température et de l'intensité des radiations implique un mécanisme radicalaire. Le nombre maximum d'unités monomériques converties en polymère pour une absorption d'énergie de 100 électron-volts, $G(M)$ est de 108.000 et de 7.600 respectivement dans la polymérisation du propylène et de l'heptène; donc les chaînes cinétiques sont longues. Cependant le degré de polymérisation moyen en nombre DP_n est bas, la valeur maximum étant de 75 dans les deux polymérisations. Dans la polymérisation du propylène, le transfert sur monomère limite DP_n; la constante de transfert devient plus importante quand la température augmente ou quand la pression diminue. Dans la polymérisation de l'heptène DP_n est déterminé à la fois par les réactions du transfert et de terminaison. Dans cette dernière polymérisation, R_p et DP_n commencent tous deux par augmenter et puis diminuent ensuite lorsqu'on augmente la température à pression constante parce que la vitesse de dépolymérisation devient appréciable à température élevée et abaisse la valeur observée de R_p.

Zusammenfassung

Es wurden mehrere Strahlungspolymerisationsreaktionen bei Drucken zwischen 5000 und 17000 Atmosphären und Temperaturen zwischen 20°C und 275°C untersucht. Die eingehendsten Untersuchungen wurden an Propylen und *n*-Tetradekafluorhepten-1 durchgeführt. Bei beiden Monomeren steht die Änderung der Polymerisationsgeschwindigkeit R_p mit Temperatur und Strahlungsintensität mit einem radikalischen Mechanismus in Einklang. Die maximale Zahl der pro 100 eV absorbierter Energie umgesetzten Monomermoleküle, $G(M)$, ist bei der Polymerisation von Propylen bzw. des Heptens 108000 bzw. 7600, d.h. die kinetischen Ketten sind lang. Das Zahlenmittel des Polymerisationsgrades, DP_n, ist jedoch niedrig, u.zw. in beiden Fällen maximal etwa 75. Bei der Polymerisation von Propylen wird DP_n durch Übertragung mit dem Monomeren begrenzt. Die Übertragungskonstante nimmt mit steigender Temperatur und abnehmendem Druck ab. Bei der Polymerisation des Heptens wird DP_n sowohl durch Übertragung als auch durch den Abbruch bestimmt. Bei der letzteren Polymerisation nehmen sowohl R_p als auch DP_n zuerst zu und sinken dann beim Ansteigen der Temperatur bei konstantem Druck, da bei hoher Temperatur die Depolymerisationsgeschwindigkeit von merklicher Grösse wird und das beobachtete R_p erniedrigt.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1161–1171

Polymerization of Chloroprene. I

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1. INTRODUCTION

More than thirty years ago Carothers[1] observed that ultraviolet irradiation of chloroprene monomer may yield an unusual granular form of the polymer which has the property of continuing growth when exposed to pure monomer. This polymeric form is crosslinked and insoluble, and has become known as "popcorn" polymer; its subsequent growth without apparent external initiation is known as "seeded" polymerization. Such seeded polymerizations will be discussed in a future publication; for the present we merely note that a characteristic frequently observed[2] is that the weight of the polymer seed increases exponentially with time, i.e., the rate of polymerization (in moles per second per seed) exhibits acceleration.

Since popcorn seeds are conveniently prepared by irradiating chloroprene vapor, it is apparent that a study of the kinetics of the initial polymerization under such conditions, followed by study of any dark reaction when the ultraviolet source is removed, may yield information of value in interpreting the formation of polymer with popcorn characteristics. This paper describes preliminary work directed towards this end. The system is complicated by the fact that the polymerization proceeds heterogeneously in the polymer gel which is rapidly formed on the wall of the vessel; no cloud of polymer is observed in the gas phase at any stage.

The first quantitative study of the polymerization of chloroprene vapor under ultraviolet irradiation was conducted by Bolland and Melville,[3] who reported that a dark reaction was observed provided that irradiation had initially proceeded for about 1500 min., after which time the centers of polymerization appear to persist for long periods. Shantarovich and Medvedev,[4] who studied the ultraviolet initiated bulk polymerization of chloroprene, also observed dark reactions, the characteristics of which depended upon the previous light history. In particular they suggest that with their reaction conditions, initial irradiation periods of greater than 300 min. cause highly crosslinked infusible (ω) polymer to be produced during the following dark reaction, whereas initial irradiation periods of less than 300 min. cause slightly branched elastic (μ) polymer to be formed during the subsequent dark reaction. Since only the ω-polymer shows characteristic popcorn growth, it appears that in the bulk polymerization of chloroprene, some minimum initial period of irradiation is required before typical pop-

corn behavior may be expected, even though dark reactions are observed after shorter periods of irradiation.

2. EXPERIMENTAL

Monomer Purification and Criteria of Purity

The crude chloroprene (Distillers Co. Ltd.,) contained inhibitors (0.2% *tert*-butyl catechol, 0.2% thiodiphenylamine) and other impurities. Since the monomer forms a peroxide with molecular oxygen,[5] air must be excluded in the purification and handling of the monomer. Accordingly, the crude monomer was first fractionally distilled under nitrogen at reduced pressure, (b.p. 36.5°C. at 300 mm.), and the middle fraction transferred, without exposure to air, to a high vacuum line where it was degassed and again fractionally distilled. To ensure removal of any peroxides or other initiators still present, the middle fraction was then partially prepolymerized. The most effective procedure was found to be about 8 hr. irradiation with a Hanovia UVS 500 lamp, which caused approximately 10% conversion. The remaining monomer was then distilled into a storage vessel cooled by liquid nitrogen, and the prepolymerization procedure repeated on each sample prior to experimental study.

The absence of impurity peaks in a gas chromatographic analysis of the monomer provided a convenient initial criterion of monomer purity. An additional criterion used throughout this work was to check that the purified monomer sample reproduced a standard thermal rate of bulk liquid-phase polymerization at 30°C. This corresponded to the minimum limiting rate of 0.047%/hr. observed for a number of experiments using different periods of prepolymerization; for periods shorter than those described above, the thermal rate is artificially high, presumably due to peroxide impurity. The reproducible thermal rate achieved with pure monomer was in fact measured dilatometrically as a function of temperature over the range 20–47°C.; the observed activation energy was 21.2 kcal./mole, which is comparable with the value 20.2 kcal./mole reported by Medvedev et al.[6]

Polymerization Conditions

Irradiation vessels were constructed from Pyrex glass and well cleaned with chromic acid before use. They were connected to the high vacuum apparatus via small-bore tubing, and thence to the monomer reservoir. During a run the reaction vessel was sealed by means of a mercury cut-off, which also served as a manometer, the reference side being evacuated by the vacuum line. The difference in mercury levels was read by a cathetometer. Reaction vessels were mounted within a thermostatically controlled water bath at 31.0°C., in a reproducible position with respect to the ultraviolet lamp. A medium-pressure mercury quartz lamp (125w Osram MB/U) was used as the ultraviolet source; the electrical supply was taken from a constant-voltage transformer, and incorporated a G.E.C.

Z1832H choke and a G.E.C. 10 μF Z1750 condenser. A Chance OXl optical filter was used to reduce the wavelength band to 3000–3900 A.

In subsequent sections the polymerization reactions are classified as follows: (*1*) initial light reactions (here the clean reaction vessel has been freshly filled with monomer vapor, and is subjected to ultraviolet irradiation); (*2*) secondary light reactions (polymerization which occurs when irradiation is resumed after a dark reaction); (*3*) dark reactions (any reaction which occurs in the absence of ultraviolet irradiation, subsequent to a light reaction).

3. RESULTS AND DISCUSSION

The pressures at the start of the initial light reactions covered the range 122–155 mm., and experiments varying in duration from 580 to 5000 min. have been studied. In all cases the pressure was observed to decrease nonlinearly with time, while a layer of polymer was seen to form on the side of the reaction vessel closest to the light source. Subsequent dark reactions were observed in every case; usually the dark rate was very much slower than the preceding light rate, though in two cases the dark rate was quite comparable with the preceding light rate. In most experiments, secondary light reactions and subsequent dark reactions were also studied. For the three kinds of polymerization, the pressure–time data were analyzed in an attempt to elucidate the kinetics of the processes.

Initial Light Reactions

Homogeneous gas-phase reaction schemes may obviously be discounted, since the polymerization is observed to take place heterogeneously in the condensed phase. Moreover, since dark reactions are observed, it appears that radical occlusion must be occurring. With this in mind, a nonstationary-state scheme has been proposed, in which highly occluded radicals grow entirely in the condensed phase. The basic assumption is that radical termination is so hampered in the gel that termination reactions may be virtually neglected, and the number of radicals will increase at a rate determined only by the rate of initiation.

If the light intensity is assumed constant in the condensed phase, and the monomer concentration (in moles per liter of condensed phase) is proportional to the pressure of monomer vapor above the condensed phase, the rate of initiation (in moles per liter of condensed phase per second) will be proportional to the monomer pressure. The rate of increase of the total number of moles of radicals in the condensed phase at any time will therefore be proportional to the product of the monomer pressure and the volume of the condensed phase at that time. Since the total decrease in pressure at any time is a measure of the volume of the condensed phase at that time, we may write

$$dR\cdot/dt = \alpha P(P_0 - P) \tag{1}$$

where $R\cdot$ is the number of moles of radicals in the condensed phase (i.e., the number of moles of free radicals in the total system), P_0 is the initial monomer pressure, P is the pressure after time t, and α is a constant.

If the ratio of monomer to polymer in the condensed film is constant or small, the rate of decrease of pressure for the constant volume gas system is proportional to the rate of polymerization in moles per second per system, which is equal to the rate of polymerization per mole of free radicals multiplied by the total number of moles of radicals in the system. Thus if the propagation rate constant k_p is expressed in the units liters of condensed phase per mole per second, and the monomer concentration [M] in moles per liter of condensed phase, the rate in moles per second per system is

$$-dM/dt = k_p[\mathrm{M}]R\cdot$$

Since the monomer concentration in the condensed phase has been assumed proportional to P, we can write

$$-dP/dt = \beta PR\cdot \tag{2}$$

where β is a constant. Dividing eq. (1) by eq. (2) yields

$$-dR\cdot/dP = (\alpha/\beta)\,(P_0 - P)/R\cdot$$

Integrating from zero to $R\cdot$, and P_0 to P, to find the number of moles of radicals at time t when the pressure is P, we obtain

$$R\cdot = \gamma\,(P_0 - P) \tag{3}$$

where γ is a constant equal to $(\alpha/\beta)^{1/2}$. Thus the number of radicals in the system is proportional to $(P_0 - P)$; with the above assumptions this means that the number of free radicals is proportional to the amount of polymer formed.

Substituting eq. (3) into eq. (2) we obtain for the rate of decrease of pressure in the system:

$$-dP/dt = (\alpha\beta)^{1/2}\,P(P_0 - P) \tag{4}$$

If it is assumed that this rate equation applies after a time t_1 when the pressure is P_1, integration from P_1 to P and t_1 to t gives

$$\ln\,[(P_0 - P)/P] = \ln\,[(P_0 - P_1)/P_1] + P_0\,(\alpha\beta)^{1/2}\,(t - t_1)$$

or

$$\ln\,(\Delta P/P) = \text{const} + P_0(\alpha\beta)^{1/2}t \tag{5}$$

In Figure 1, $\log\,(\Delta P/P)$ is plotted against t for a number of initial light runs. Since the plots show satisfactory linearity from the earliest stages, the above scheme may be assumed to apply throughout the observable reaction. Additional confirmation of this kinetic mechanism is provided in the following section, where the same basic assumptions are made.

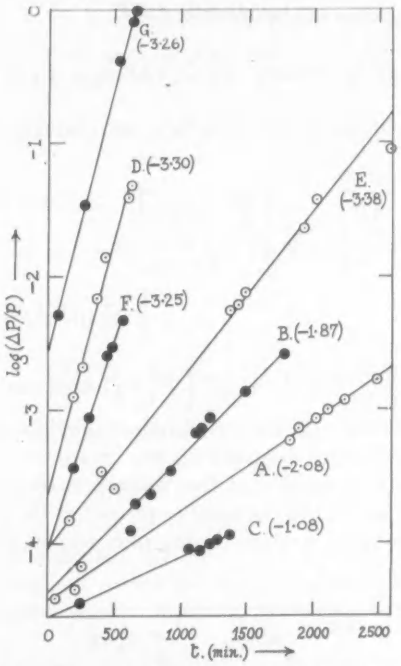

Fig. 1. Initial light reactions plotted according to eq. (5). Plots are displaced vertically to improve clarity; the actual intercepts on the log $(\Delta P/P)$ axis are shown in parentheses.

Secondary Light Reactions

Suppose $(\Delta P_L)_1$ is the total decrease in pressure during an initial light run, and $(\Delta P_D)_1$ is the additional decrease in pressure during the following dark reaction. The decrease in pressure during subsequent light and dark reactions may be represented by

$$(\Delta P_L)_2, (\Delta P_D)_2, \ldots, (\Delta P_L)_x, (\Delta P_D)_x$$

The kinetic scheme of the previous section may be applied to secondary light reactions in the following way, by assuming that the number of radicals created during a light run is proportional to ΔP during that run, and that the number of radicals remains constant during dark runs.

Thus for the nth light reaction, at the start:

$$t = 0, P = P_n, R\cdot = \gamma \sum_1^{n-1} (\Delta P_L)_x$$

and during the reaction:

$$t = t, P = P, R\cdot = \gamma \left[\sum_1^{n-1} (\Delta P_L)_x + P_n - P \right]$$

and the rate at any time will be given by:

$$-dP/dt = (\alpha\beta)^{1/2} P\left[\sum_{1}^{n-1} (\Delta P_L)_x + P_n - P\right] \quad (6)$$

Integrating from P_n to P and zero to t, and putting $(P_n - P) = \Delta P$, we obtain

$$\ln\left[\frac{\sum_{1}^{n-1} (\Delta P_L)_x + \Delta P}{P}\right] = \ln\left[\frac{\sum_{1}^{n-1} (\Delta P_L)_x}{P_n}\right] + \left[\sum_{1}^{n-1} (\Delta P_L)_x + P_n\right](\alpha\beta)^{1/2} t \quad (7)$$

In Figure 2, $\log\left\{\left[\sum_{1}^{n-1} (\Delta P_L)_x + \Delta P\right]/P\right\}$ is plotted against t for a number of secondary light runs. The linearity obtained provides acceptable evidence for the kinetic mechanism discussed above. Since the treatment here further assumes that the number of free radicals is constant during a dark reaction, and corresponds to the number present at the end of the previous light reaction, the dark reactions in the next section are considered from this point of view.

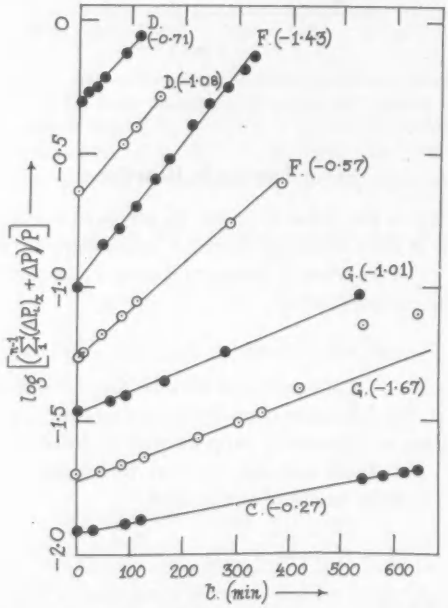

Fig. 2. Secondary light reactions, plotted according to eq. (7). Plots are displaced vertically to improve clarity; the actual ordinates at $t = 0$ are shown in parentheses. The time scale should be doubled for plot C.

Dark Reactions

Using the same symbols as in the previous section, for the nth dark reaction we may write at the start:

$$t = 0, P = P_n', R\cdot = \gamma \sum_1^n (\Delta P_L)_x$$

and during the reaction:

$$t = t, P = P, R\cdot = \gamma \sum_1^n (\Delta P_L)_x$$

and the rate equation will now be:

$$-dP/dt = (\alpha\beta)^{1/2} P\left[\sum_1^n (\Delta P_L)_x\right] \tag{8}$$

Integrating from P_n' to P and zero to t gives

$$\ln P = \ln P_n' - (\alpha\beta)^{1/2}\left[\sum_1^n (\Delta P_L)_x\right]t \tag{9}$$

In Figure 3, log P is plotted against t for a number of dark reactions. Good linearity is obtained, except for the anomalous cases marked C and E, which are discussed below. Equation (9) suggests that the gradients

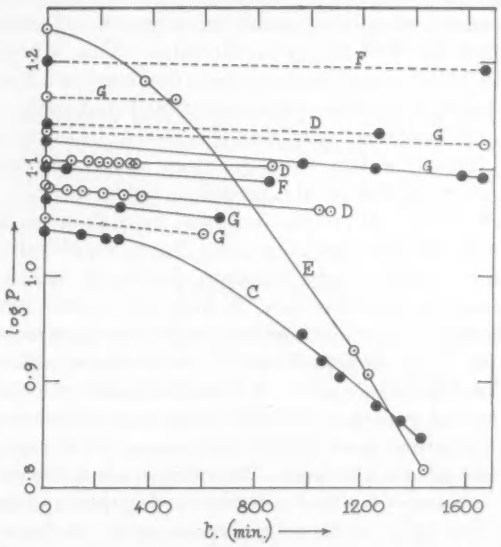

Fig. 3. Dark reactions, plotted according to eq. (9). In five of the dark reactions only the initial and final pressure readings were taken. (The gradients of these five plots are shown as open circles in Fig. 4.)

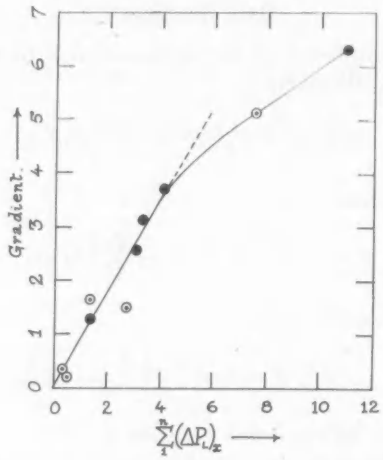

Fig. 4. Dark reactions: gradients of the rate plots (see Fig. 3) plotted against the corresponding values of $\sum_1^n (\Delta P_L)_x$.

of the linear plots should be proportional to the values of $\sum_1^n (\Delta P_L)_x$ for the corresponding reactions; this is verified in Figure 4. The results indicate that as the amount of polymer phase increases, the effective number of radicals becomes less than the predicted value. This is probably due to the eventual diffusion control of the propagation reaction; the more deeply embedded radicals are now less readily accessible to monomer.

The anomalous dark reactions C and E appear to be following a different mechanism. Indeed, in these cases the mean rate of decrease of pressure was comparable with that of the preceding light reactions, whereas for the other dark reactions the mean rate was more than ten times smaller than that of the preceding light reaction. Purely empirical application of the scheme for secondary light reactions (involving radical generation), to these anomalous reactions does in fact give rather better linearity (Fig. 5). The results therefore appear to lead to the unexpected conclusion that during these dark reactions C and E, the number of radicals is actually increasing at an appreciable rate. It is interesting to note that the characteristic exponential growth of a seeded popcorn polymerization may also be explained by assuming an increase in the number of radicals following the increase in weight of the seed. With this in mind, the polymeric films C and E were carefully examined to assess whether their appearance differed from that of the films in the other experiments. In films C and E, a number of hard nodules could be observed within the skin of the polymer. Possibly these constituted sites at which popcorn-type polymerization had started to occur. An examination of the experimental conditions of these

runs has not revealed any clear reason why such behavior should have been favored in these two cases. However, the initial light reactions C and E had been allowed to proceed for a longer period (1385 min. and 4350 min., respectively) than in any of the other cases (greatest period 680 min.) in which a subsequent dark reaction was followed. We therefore conclude tentatively that popcorn-type centers are completely absent in

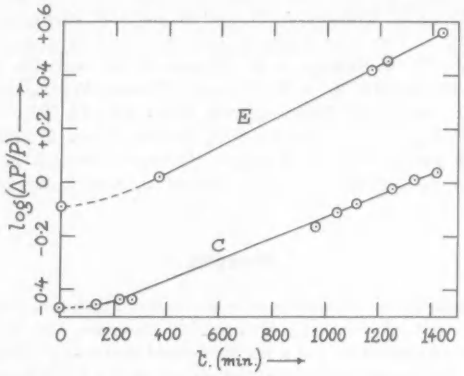

Fig. 5. Dark reactions C and E plotted according to eq. (7). The gradients are comparable with those of the slower reactions in Fig. 2. (In each case these dark reactions directly followed the corresponding initial light reaction; $\Delta P'$ in the expression for the ordinates here is the sum of $(\Delta P_L)_i$ for the light reaction and ΔP for the dark reaction.)

gas-phase heterogeneous polymerizations of chloroprene unless the initial irradiation period exceeds some minimum value, in our system between 10 and 20 hr. approximately. It will be recalled (section 1) that a similar restriction appears to apply to the formation of popcorn centers in the bulk polymerization of chloroprene.

4. CONCLUSIONS

The results of the present work can best be interpreted by assuming that the polymerization occurs in a condensed film on the surface of the reaction vessel, and that this film forms virtually at the start of the polymerization. The monomer concentration within the film is proportional to the pressure of monomer vapor above it, and the radicals are occluded within the film. In the light reactions the number of radicals within the film continually increases, and is proportional to the amount of polymer formed. In dark reactions which follow a short light reaction, the number of radicals remains constant and simple kinetics are followed provided that the film is not too thick, when the addition of monomer to some of the radicals probably becomes diffusion controlled. Dark reactions which follow a more

lengthy light reaction proceed by a different mechanism which appears to involve the generation of radicals; in these cases it is believed that popcorn-type polymerization has started to occur.

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Synopsis

Ultraviolet irradiation of chloroprene may produce solid popcorn polymer. As a preliminary to the study of popcorn polymerization processes, the heterogeneous polymerization on the irradiated wall of a reaction vessel containing chloroprene vapor has been examined. The results suggest that radical occlusion occurs once an initial polymer film is formed, the number of such radicals being proportional to the amount of polymer formed. The effective monomer concentration in the polymer phase is proportional to the pressure of gaseous monomer. The polymerization continues when the source of irradiation is removed; in some cases these "dark" reactions show some of the characteristics of popcorn growth.

Résumé

L'irradiation ultraviolette de chloroprène peut produire un polymère solide gonflé. Avant d'étudier le processus de cette polymérisation, on a effectué la polymérisation hétérogène sur la paroi irradiée d'un tube de réaction contenant du chloroprène en phase vapeur. Les résultats montrent que l'occlusion radicalaire s'effectue lorsqu'un film initial du polymère est formé, le nombre de tels radicaux demeurant proportionnel à la quantité de polymère formé. La concentration monomérique effective dans la phase polymérique est proportionnelle à la pression gazeuse du monomère. La polymérisation continue après arrêt de l'irradiation; dans certains cas ces réactions "à l'obscurité" montrent certaines caractéristiques de la croissance des grains.

Zusammenfassung

Bei der UV-Bestrahlung von Chloropren können feste Popcornpolymere entstehen. In Vorversuchen zur Popcornpolymerisation wurde die heterogene Polymerisation an der bestrahlten Wand eines Chloroprendampf enthaltenden Reaktionsgefässes untersucht. Die Ergebnisse lassen erkennen, dass, sobald einmal ein Polymerfilm gebildet wurde, Radikaleinschluss auftritt, wobei die Zahl dieser Radikale der Menge des gebildeten Polymeren proportional ist. Die effektive Monomerkonzentration in der Polymerphase ist dem Druck des gasförmigen Monomeren proportional. Bei Entfernung der Lichtquelle geht die Polymerisation weiter; in einigen Fäl'en zeigt diese Dunkelreaktion das charakteristische Verhalten des Popcorn-Wachstums.

Discussion

A. Chapiro (*C.N.R.S., Bellevue, S. et O., France*): Avez-vous effectivement observe la formation de globules de polymère popcorn? En effet la déviation de la loi cinétique observée pourrait être due à une variation continue de la "constante" de terminaison, celle-ci devenant de plus en plus petite au fur et à mesure de l'avancement de la réaction.

R. S. Lehrle: In the anomalous dark reactions, the nodules referred to are believed to be popcorn centers, and could be detected visually.

Dr. Chapiro's hypothesis cannot be applied here, since the simplest kinetic scheme which fits our data is the one described, which contains no termination term. The introduction of such a term would necessitate the insertion of *ad hoc* terms into the scheme, and we feel that this could not be justified.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1173–1193

Grafting of Styrene onto Teflon and Polyethylene by Preirradiation

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It has been shown[1,2] that the chain propagation reaction becomes practically never diffusion controlled in free radical polymerization, whereas termination is practically always diffusion-controlled. This facilitates the understanding and treatment of polymerization reactions under unusual conditions, as graft copolymerization.

Recently we have given a brief account[3] of graft copolymerization of styrene onto polytetrafluoroethylene (Teflon) films preirradiated in air. In the present paper we give some additional data and calculations on the same system and results of the grafting onto polyethylene pellets.

I. GRAFTING ONTO TEFLON

Experimental

Teflon film of 0.24 mm. thickness and specific gravity of 2.20 was used. (We obtained a similar set of data with a film of 0.10 mm. thickness and of another grade.) Irradiation was performed in air in a 400-c. Co^{60} source; irradiation time was 72 hr.

Different doses were obtained by varying the intensity. Graft polymerization was performed by placing 1.5 g. irradiated Teflon film in a dilatometer of 20 ml. capacity, and filled with doubly distilled styrene. The dilatometer was evacuated and sealed. The conversion of styrene was followed dilatometrically at different temperatures, the homopolymerization checked by refractive index, and the final value of grafting by weight measurement. The results of grafting in styrene–benzene solutions and some further control measurements were performed separately in evacuated and sealed test-tubes.

The penetration of grafting was checked on the test-tube experiments by measuring the optical density across microsections of the grafted and colored films.

It was shown by ESR measurements of R. Marx (Orsay) and E. Rhyter (Sacly), that there is a linear dependence between dose and radical concentration below 10 Mr.

Results

The grafting of styrene onto Teflon preirradiated in air is of the trapped free radical type, as it takes place even at low temperatures.

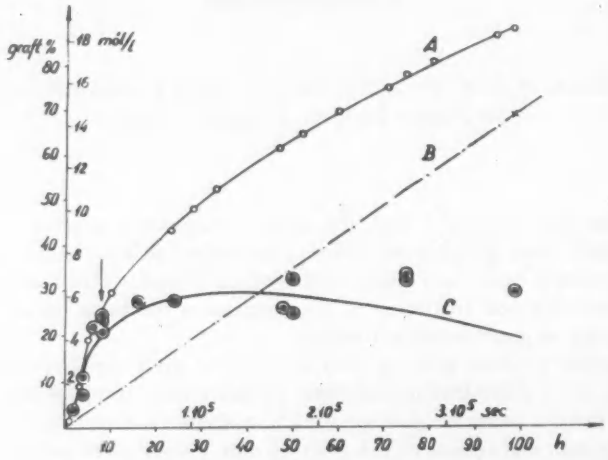

Fig. 1. Conversion vs. time for grafting of styrene onto preirradiated Teflon (dose = 8.6 Mr; T = 50°C.): (A) total dilatometric conversion; (B) homopolymerization; (C) net grafting (A − B); (⊙) grafting determined by weight increase. Grafting through is indicated by an arrow. Conversion in % grafting = [(weight of grafted copolymer/weight of original polymer) − 1] × 100 or in mole styrene/l. Teflon.

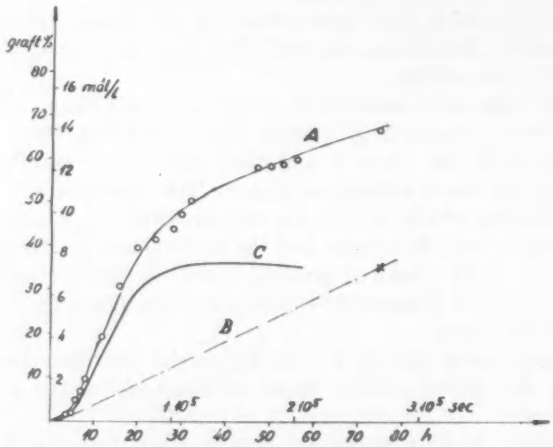

Fig. 2. Conuersion vs. time for grafting of styrene onto preirradiated Teflon (dose = 8.6 Mr; T = 30°C.). Symbols as for Fig. 1.

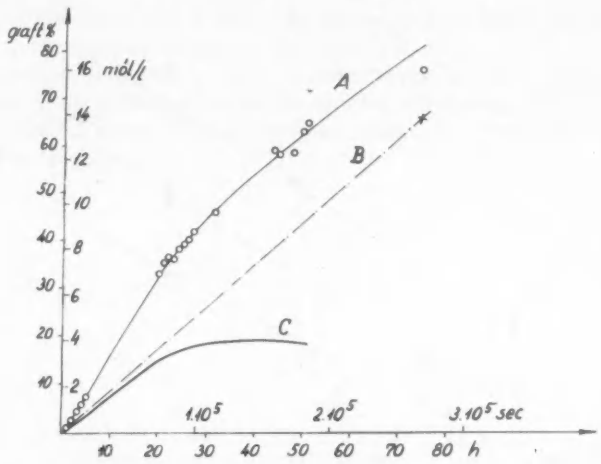

Fig. 3. Conversion vs. time for grafting of styrene onto preirradiated Teflon (dose = 0.68 Mr; T = 50°C.). Symbols as for Fig. 1.

The course of grafting has been found in each experiment to be the same: after an induction period (which is sometimes hard to observe), there is a nearly linear portion of rate v, after which grafting becomes practically stopped at a limiting value g. Figures 1–4 show some typical curves.

The induction period decreases with increasing dose (or radical concentration) and temperature.

The rate v is proportional to a power of somewhat greater than 0.5 of the dose or radical concentration (Fig. 5) and has an overall activation energy of E_v = 8 kcal./mole.

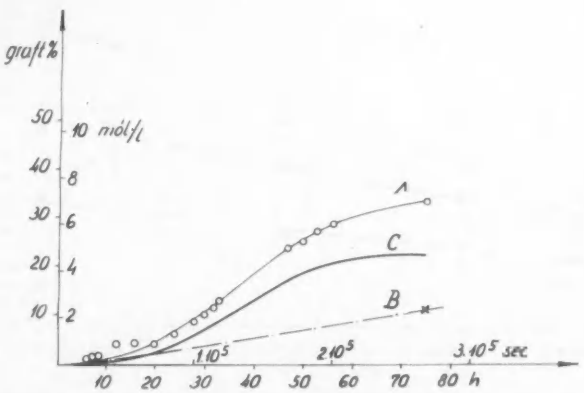

Fig. 4. Conversion vs. time for grafting of styrene onto preirradiated Teflon (dose = 0.68 Mr; T = 30°C.). Symbols as for Fig. 1.

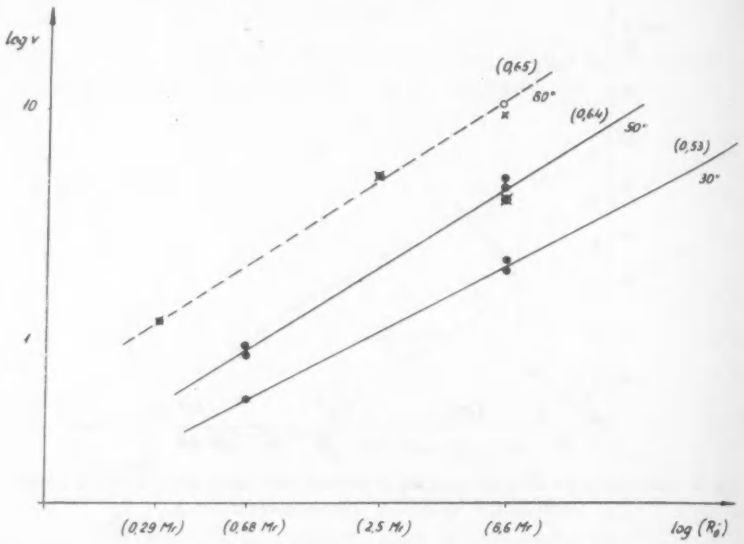

Fig. 5. Dependence of the rate of grafting onto Teflon on radical concentration at different temperatures: (●) from dilatometric measurements; (×, ○) from weight measurements (two films of different qualities).

The height of the limiting value g increases with the logarithm of radical concentration (Fig. 6) and decreases with increasing temperature (E_g = 4.2 kcal./mole).

The grafting proceeds from the surface into the inner layers of the film

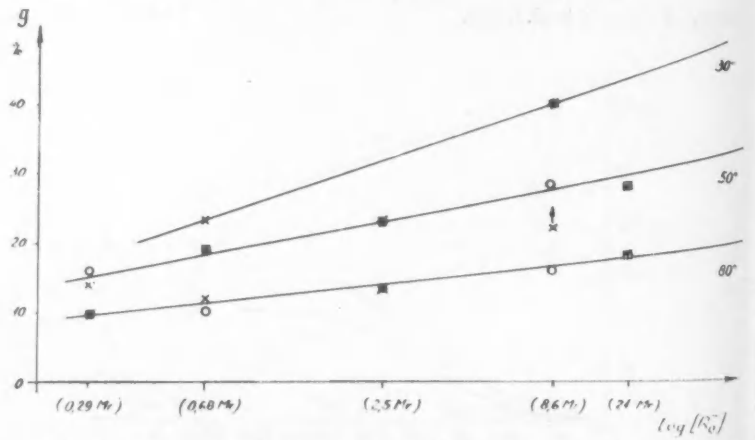

Fig. 6. Dependence of the limiting value of grafting onto Teflon on the logarithm of the radical concentration: (×, ○) from weight measurements (two films of different qualities).

(Fig. 7). The upper end of the linear portion of the grafting curves corresponds to the grafting-through of the films (Fig. 1).

The grafting rate is proportional on the average to the 1.1 power of the monomer concentration, whereas the limiting value of grafting is proportional to the 0.7 power of monomer concentration in styrene–benzene mixtures (Figs. 8 and 9).

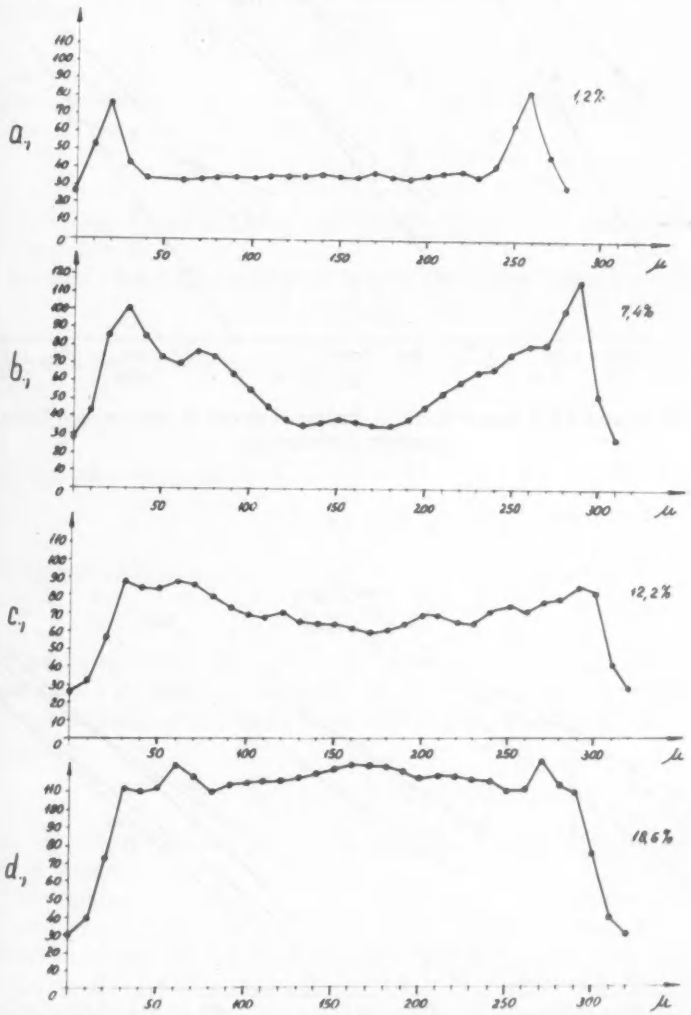

Fig. 7. Movement of the grafting front in preirradiation grafting onto Teflon films from optical densitometric curves of colored microsections at various grafting times (dose = 0.68 Mr; $T = 50°C.$): (*a*) 4 hr.; (*b*) 8 hr.; (*c*) 12 hr.; (*d*) 48 hr.

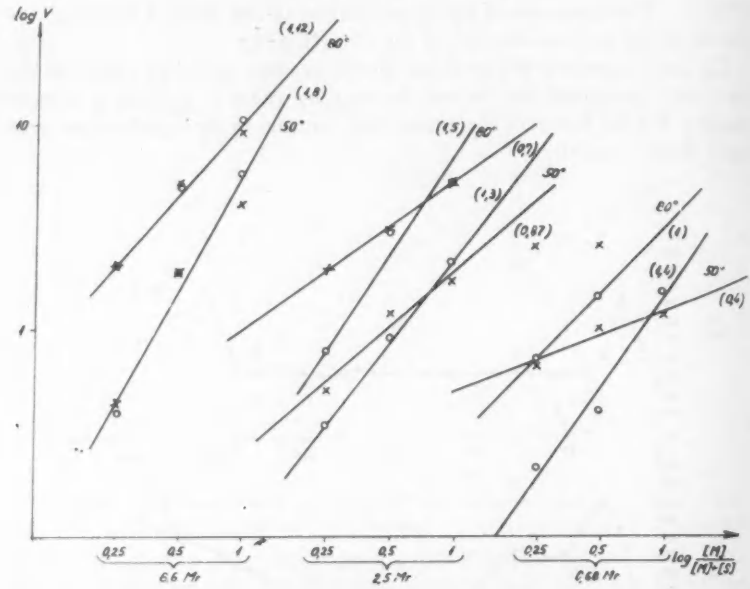

Fig. 8. Dependence of linear velocity of grafting of styrene in benzene onto Teflon on monomer concentration.

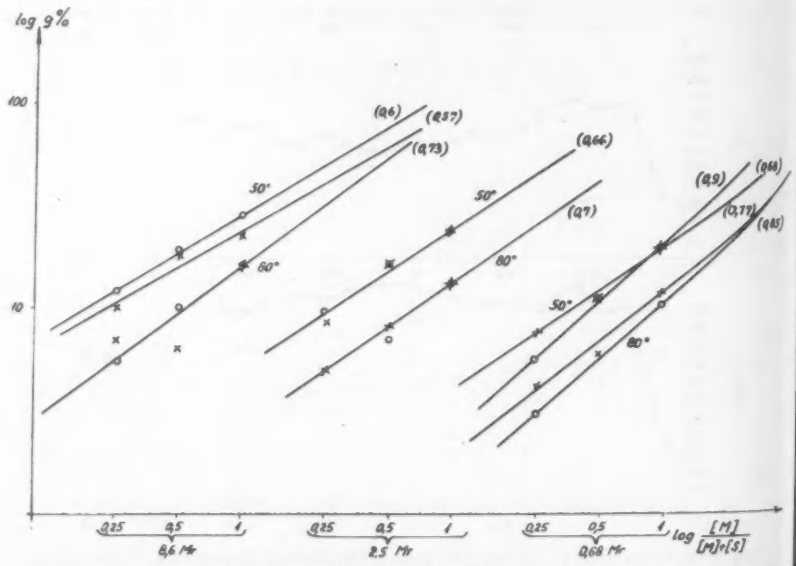

Fig. 9. Dependence of limiting value of grafting of styrene in benzene onto Teflon on monomer concentration.

Discussion

Initiation in graft copolymerization onto trapped free radicals corresponds to the addition of the first monomer molecule. The rate-determining step of this process is the diffusion of monomer into the ungrafted parts of the film.

The rate of initiation is proportional to the concentration of the free radicals,

$$v_i = k_i [R_0\cdot]$$

while k_i itself is proportional to the rate v_f at which the grafting front proceeds into the inner parts of the film:

$$k_i \sim v_f = \bar{r}/t$$

where t is the time of diffusion to a distance $\bar{r}$, and $\bar{r}$ is the mean distance between radicals.

The time needed for the diffusion is, from the Stokes-Einstein relation,

$$t = \bar{r}^2/6D$$

where D is the diffusion coefficient,
so that

$$v_f \sim 1/\bar{r}$$

and, as $\bar{r}$ depends on $[R_0\cdot]^{-1/3}$

$$k_i = k_i' [R_0\cdot]^{1/3}$$

and the rate of initiation is

$$v_i = k_i' [R_0\cdot]^{4/3} \tag{1}$$

For the propagation reaction, on the other hand, the monomer has to permeate the already grafted, swollen parts. This process is very rapid.

It follows from eq. (1), that if chain termination is bimolecular, the rate of grafting is

$$v = (k_i'^{1/2} k_p / k_t^{1/2}) [R_0\cdot]^{2/3} [M] \tag{2}$$

where k_p, k_t and [M] have their usual meaning. This is in fair agreement with experimental results.

The condition for a linear rate is a stationary concentration of growing chains in the polymer film. There can be no question of stationary concentration of growing chains in any particular part of the film. In the parts of the film just attained by the monomer the concentration of growing chains is high, and this concentration decreases as a result of termination. But it is possible to have a stationary concentration of growing chains for the whole of the film if the rates of initiation and termination of the chains are the same.

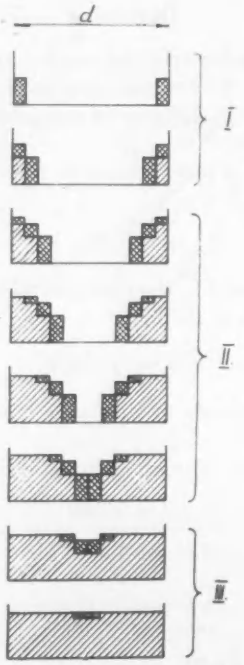

Fig. 10. Schematic representation of the progress of grafting through a thickness d of film: (*I*) induction period; (*II*) linear period; (*III*) flattening off period.

This condition can be fulfilled if the growing chains are terminated in a time shorter than that required for the grafting of the film throughout its whole thickness. The lifetime of growing chains can be approximately identified with the induction period τ. In our experiments this is 1.5 hr., where grafting-through takes 8 hr.

According to this picture, the grafting of styrene proceeds with the rate of diffusion of monomer to the hitherto ungrafted radicals into the inner parts of the film. The grafting reaction itself takes place in a relatively narrow traveling front.

The proceeding of the grafting front is schematically represented in Figure 10. It can be compared with the direct microdensitometric measurements of microsections from the grafted and colored films in Figure 7.

In each elementary thickness of the film we have a nonstationary "post-polymerization," starting from the high initial radical concentration. The limiting value of grafting g is the sum of these nonstationary processes, i.e., it is proportional to the chain length under nonstationary-state conditions. (The expression "limiting value" is in fact not quite correct, as g should increase with t, but this is not observable in the present system.)

$$g = (k_p/k_t)\ [\mathrm{M}] \log (k_t[\mathrm{R}_0\cdot]t + 1) \qquad (3)$$

As can be seen from Figure 6, g is proportional to the logarithm of the radical concentration. After a sufficiently long time t this can not be distinguished from the dependence of eq. 3.

The overall activation energy of reaction (2) is

$$E_v = E_{t/2} + E_p - E_{t/2} = 8 \text{ kcal./mole}$$

and of reaction (3)

$$E_g = E_p - E_t = -4.2 \text{ kcal./mole}$$

If E_p is, as in homogeneous nonviscous media, 7.2 kcal./mole, we have

$$E_t = 13 \text{ kcal./mole}$$

which should be related to the activation energy of diffusion of monomer into Teflon, and

$$E_t = 11.4 \text{ kcal./mole}$$

which is a very high value. If we take into account that the induction period is related to the chain termination constant by

$$\tau = 1/k_t[\mathrm{R}\cdot]$$

the experimentally found activation energy of $E_\tau = -10$ kcal./mole corresponds to $E_t = 10$ kcal./mole.

A high linear velocity followed by a limiting value of grafting was observed by various authors in grafting onto trapped free radicals.[4-11] We have shown[3] that a great part of these results can be correlated with the principles outlined above. Curves of somewhat similar form have been obtained by Chapiro in his well-known experiments[12,13] on the simultaneous grafting of styrene onto Teflon by radiation of high intensity. It can be shown, however, that the limiting value of grafting obtained in Chapiro's experiments have a completely different character. (*1*) By increasing the temperature the limiting value of grafting is increased in the case of simultaneous grafting, and decreased in the case of preirradiation grafting. (*2*) The decrease of the monomer concentration in styrene–benzene mixtures results in the same effect. (*3*) In the case of simultaneous grafting, limiting values decrease at higher intensities. In preirradiation grafting, on the other hand, the higher radical concentration obtained by higher radiation doses results in an increase of the limiting value. (*4*) In the case of simultaneous irradiation, a limiting value of grafting can only be obtained with films which have not been grafted through completely. By preirradiation grafting, each film which has attained a limiting value of grafting is completely grafted through, uniformly in most cases.

This proves, that the limitation of grafting in simultaneous irradiation has completely different reasons, namely a depletion of monomer in the Teflon films, caused by the radiation of high intensity.[12,13] Furthermore, the polystyrene enclosed in the Teflon can be swollen to a limited extent only and therefore, as a result of a rapid grafting process can even get beneath

its second order transition point. This causes a definitive cease of further grafting at the given temperature. All this is in sharp contrast to the limiting of grafting by pure kinetic factors, as in our experiments.

II. GRAFTING ONTO POLYETHYLENE

Experimental

Samples, 6 × 6 mm., were prepared from high pressure polyethylene film of 0.5 mm. thickness. Before use, the samples had been extracted for several days in 1:1 alcohol–benzene solutions. Irradiations were performed in dilatometers at room temperature under nitrogen atmosphere, with a 400-C. Co^{60} source. The intensity of the irradiation was 265 kr./hr., the total dose amounting to 0.53 Mrads. Dilatometers were filled with styrene after irradiation and sealed in the absence of oxygen. Total conversion rates were measured at 0, 10, 20, 30, 40, and 50°C., with six ampules at least at the same temperatures. The amount of grafting was determined by weight measurements made after thorough extraction of the samples in benzene at room temperature.

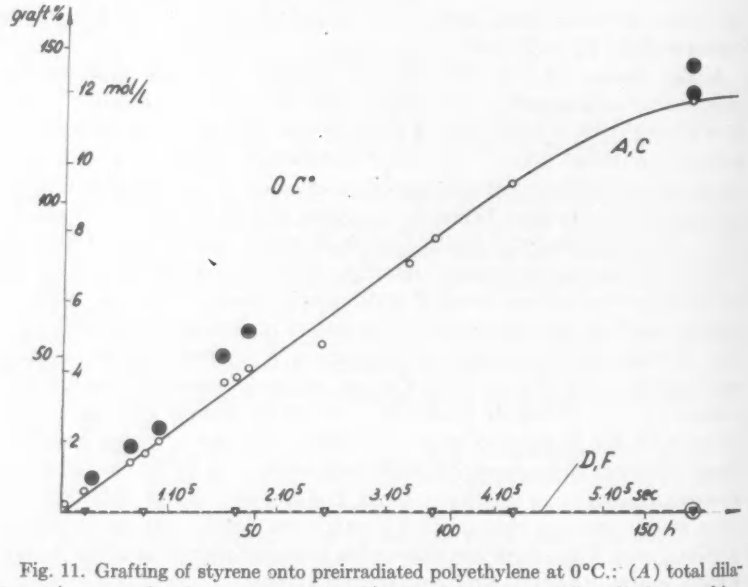

Fig. 11. Grafting of styrene onto preirradiated polyethylene at 0°C.: (*A*) total dilatometric conversion in presence of irradiated polyethylene; (*C*) radiation grafting (difference of curve *A* and calculated thermal homopolymerization); (*D*) dilatometric conversion of styrene in presence of nonirradiated polyethylene; (*F*) spontaneous grafting (difference of curve *D* and calculated thermal homopolymerization); (⊙) grafting from weight increase in preirradiated polyethylene, ● grafting from weight increase in non irradiated polyethylene.

Results

Grafting is essentially of the trapped free radical type.

The dilatometric grafting curves (C in Figures 11–16) obtained by subtracting the spontaneous homopolymerization from the total dilatometric conversion (A) have two distinct portions: grafting starts at a constant rate which is much higher than that of the spontaneous grafting (F); after a certain time, the grafting rate becomes practically the same as in the case of nonirradiated polyethylene, the slopes of the curves C and F being approximately the same.

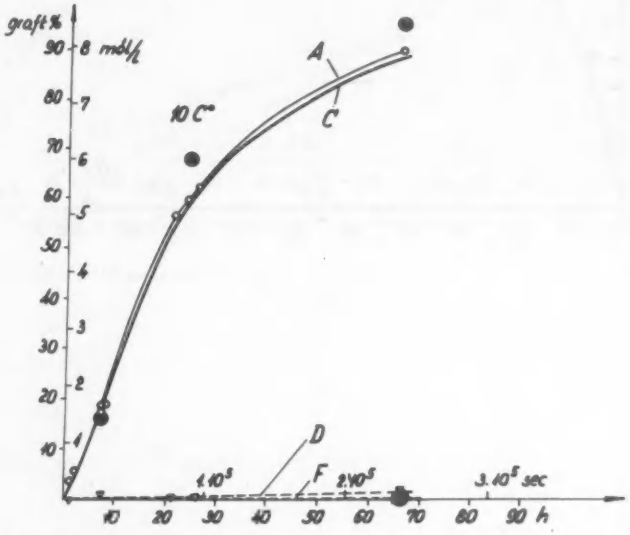

Fig. 12. Grafting of styrene onto preirradiated polyethylene at 10°C. Symbols as in Fig. 11.

The first, linear portion of the curves C (indicated by broken line in Figures 13–16) becomes steeper with increasing temperature. Its activation energy is 8.5 kcal./mole (Fig. 17).

The ordinate sections of the prolongation of the flattened part of the curves C become smaller with increasing temperature. These sections correspond to the total grafting by the trapped free radicals and are analogous to the limiting value of grafting onto Teflon g. From Figure 18 we obtain for E_g an overall activation energy of -5.3 kcal./mole.

The rate of the spontaneous grafting onto nonirradiated polyethylene is linear within the time interval investigated and increases with increasing temperature. Its overall activation energy, as calculated from Figure 19, is 12.4 kcal./mole. Chapiro[14] has found 12.6 kcal./mole for the overall

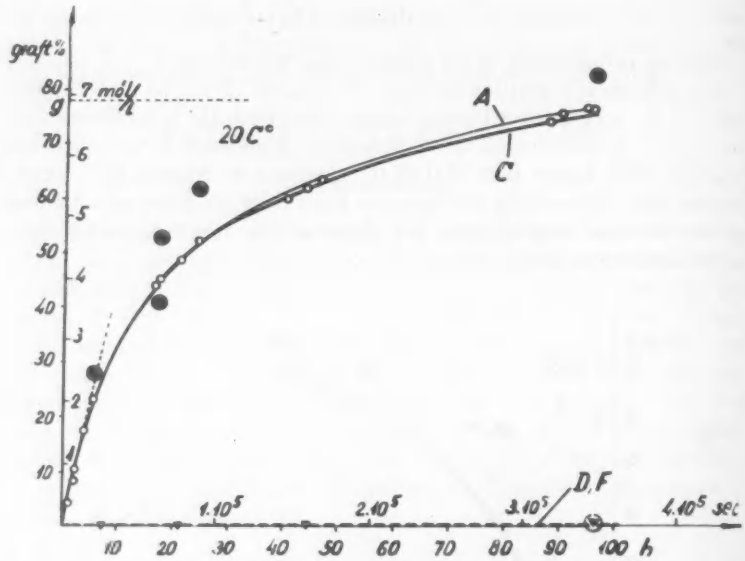

Fig. 13. Grafting of styrene onto preirradiated polyethylene at 20°C. Symbols as in Fig. 11.

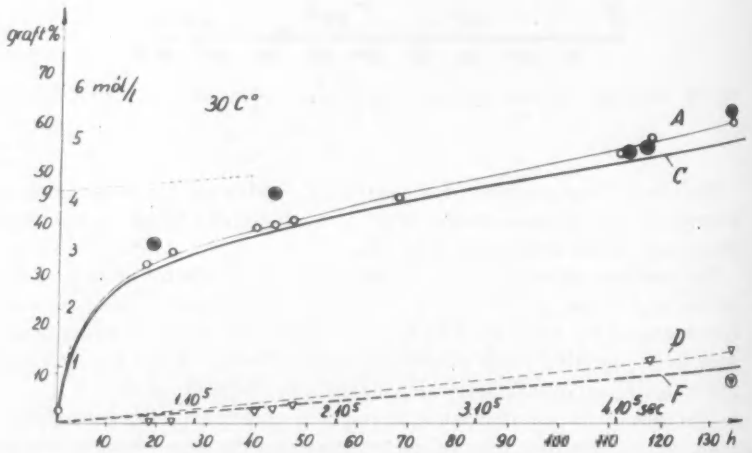

Fig. 14. Grafting of styrene onto preirradiated polyethylene at 30°C. Symbols as in Fig. 11.

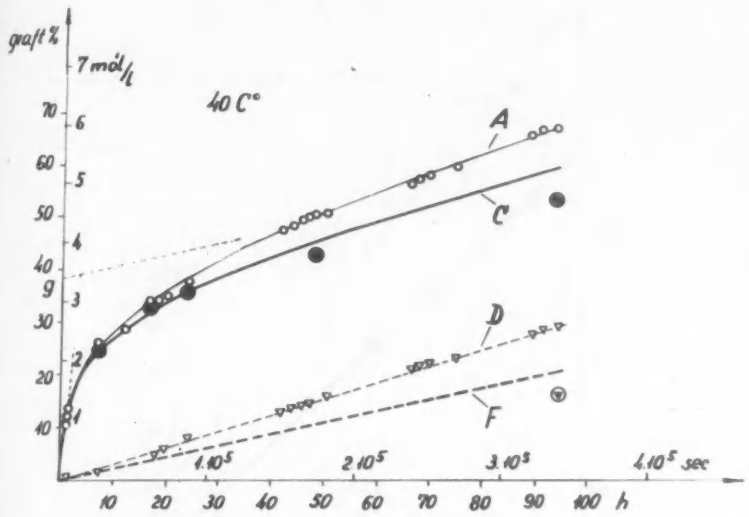

Fig. 15. Grafting of styrene onto preirradiated polyethylene at 40°C. Symbols as in Fig. 11.

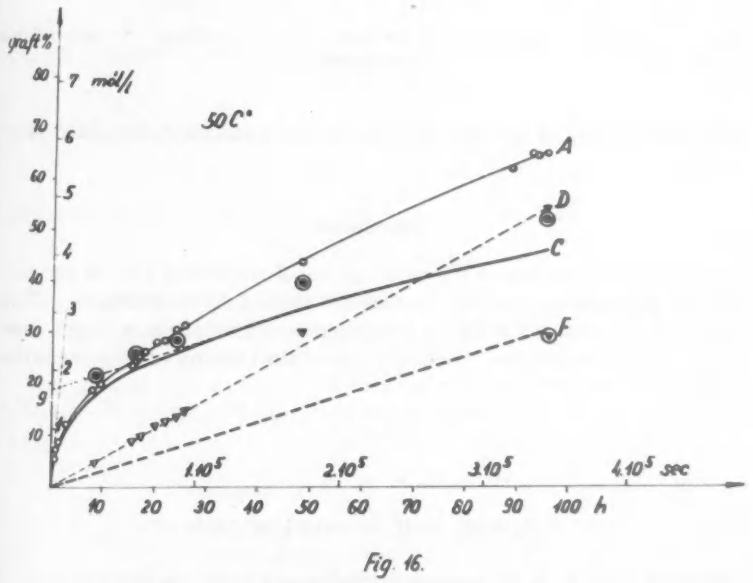

Fig. 16.

Fig. 16. Grafting of styrene onto preirradiated polyethylene at 50°C. Symbols as in Fig. 11.

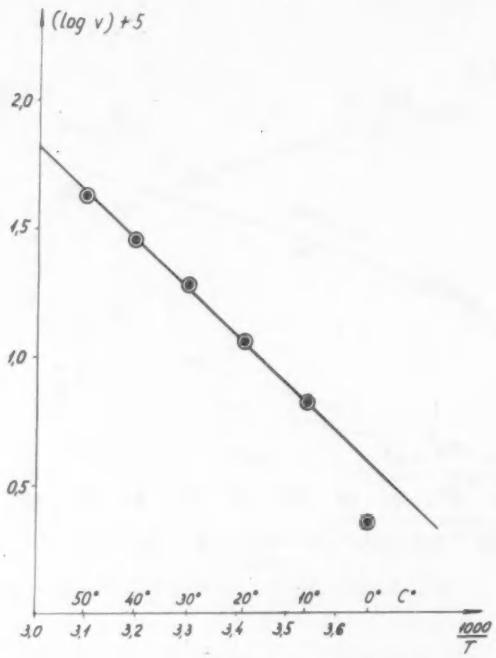

Fig. 17. Temperature dependence of the rate v of initial grafting onto preirradiated polyethylene.

activation energy of grafting of styrene onto radiation-peroxidized polyethylene.

Discussion

The ordinate sections of the prolongation of the second part of curves C can be regarded as grafting to radicals formed by irradiation. These values correspond to the post-polymerization or kinetic chain length under nonstationary conditions. As in the case of the limiting value g of grafting to Teflon,

$$g \approx k_p/k_t$$

so that

$$E_g = E_p - E_t = -5.3 \text{ kcal./mole}$$

Assuming, that E_p is the same as in nonviscous media, we have

$$E_t = 12.5 \text{ kcal./mole}$$

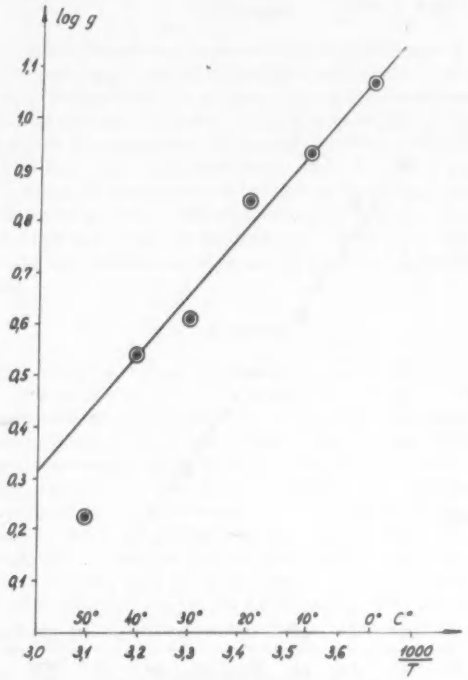

Fig. 18. Temperature dependence of the total grafting g by trapped free radicals onto polyethylene.

For the activation energy of the initial linear velocity there is found

$$E_v = E_{t/2} - E_p - E_{t/2} = 8.5 \text{ kcal./mole}$$

and so we get for the activation energy of initiation of grafting

$$E_i = 14.6 \text{ kcal./mole}$$

This is approximately the same value, as the activation energy of diffusion of xylene and similar molecules into polyethylene.[15,16] We think that these activation energies are closely connected.

The spontaneous grafting onto nonirradiated polyethylene has a linear velocity. If the quasi-stationary-state conditions can be applied here too, we have

$$E_{v,sp} = (E_{i,sp}/2) + E_p - (E_t/2) = 12.4 \text{ kcal./mole}$$

where $E_{i,sp}$ is the activation energy of the initiation of spontaneous grafting, and E_t is that of the termination.

Substituted for E_p and E_t as above we get

$$E_{i,sp} = 22.8 \text{ kcal./mole}$$

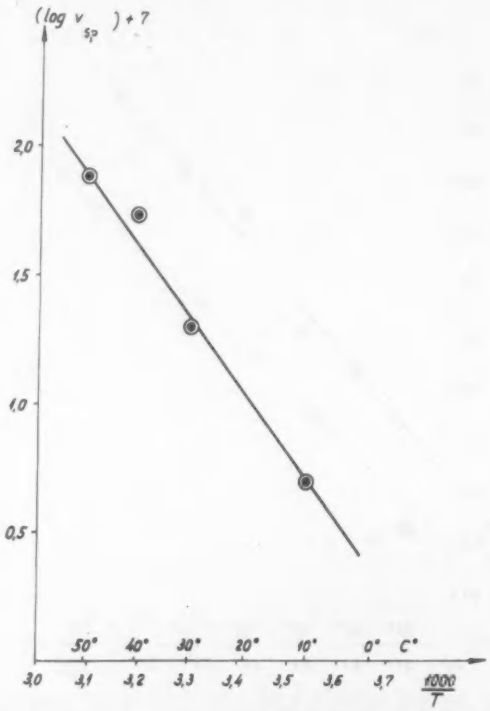

Fig. 19. Temperature dependence of the rate of the spontaneous grafting onto non-irradiated polyethylene.

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Synopsis

The use of the classical equations of polymerization kinetics gives a fair approximation for describing the grafting process on trapped free radicals in some heterogeneous systems. Initiation corresponds to the addition of the first monomer molecules to the trapped radicals. As a result of diffusion effects, the activation energies of initiation and termination are higher than expected. E_i has been found to be 13 kcal./mole for styrene in Teflon and 14.6 kcal./mole in polyethylene, while E_t is 11.4 and 12.5 kcal./mole, respectively. In Teflon, grafting is shown to begin at the surface and to take place in a relatively narrow travelling front. When the whole film is grafted through, the reaction slows down and comes to an end. In grafting onto polyethylene there is a spontaneous grafting of constant rate onto the unirradiated films, with an apparent activation energy of 12.4 kcal./mole.

Résumé

L'emploi des équations chimiques en cinétique de polymérisation a donné une bonne approximation dans la description du processus de greffage sur des radicaux libres piégés dans plusieurs systèmes hétérogènes. L'initiation correspond à l'addition des premières molécules de monomères aux radicaux piégés. Les énergies d'activation de l'initiation et de la terminaison sont, à cause des effets de diffusion, plus élevées qu'on ne s'y attendrait. On a trouvé pour E_i 13 kcal/môle pour le styrène dans le Teflon et 14.6 kcal/mole dans le polyéthylène tandis que E_t est respectivement de 11.4 et 12.5 kcal/môle. Dans le Teflon, le greffage semble commencer sur la surface et avoir lieu dans un espace mobile relativement étroit. Quand le film est greffé dans son entièreté, la réaction ralentit et prend fin. En greffant sur du polyéthylène, il ya un "greffage spontané" de vitesse constante sur les films non-irradiés avec une énergie d'activation apparente de 12.4 kcal/môle. Une étude comparative des produits greffés est en cours.

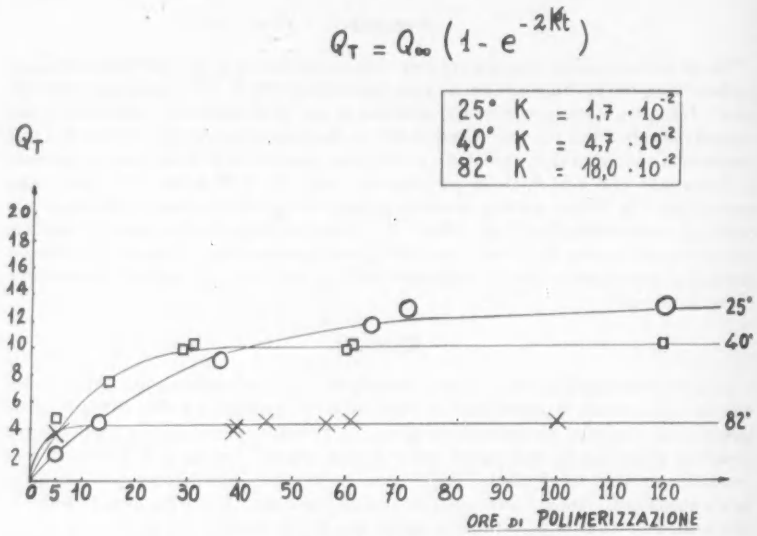
Zusammenfassung

Mit Hilfe der klassischen Gleichungen der Polymerisationskinetik ist es gelungen, die durch eingefrorenen freien Radikalen ausgelöste Pfropf-Kopolymerisation in heterogenen Systemen mit guter Annäherung zu beschreiben. Die Initiierung entspricht der Addition des ersten Monomerenmoleküls. In Folge von Diffusionseffekten fallen die Aktivierungsenergien der Initiierung und des Kettenabbruchs höher aus, als es zu erwarten wäre. Für Styrol in Teflon wurde E_i = 13 kcal/Mol, und in Polyäthylen 14,6 kcal/Mol gefunden; die entsprechenden Werte für E_t sind 11,4, bzw. 12,5 kcal/Mol. Es wurde gezeigt, dass die Propfung im Teflon auf der Oberfläche beginnt und sich in einer verhältnissmässig schmalen, wandernden Front abspielt. Wenn der ganze Film durchgepfropft ist, verlangsamt sich zuerst die Reaktion und hört dann auf. In der Propfung auf Polyäthylen ist eine "spontane Propfung" konstanter Geschwidigkeit auf unbestrahlte Folien zu bemerken, deren globale Aktivierungsenergie 12,4 kcal/Mol beträgt.

Discussion

C. Rossi (*Instituto di Chimica Industriale, Geneva, Italy*): Nous avons fait des mésures de greffage de styrène sur lamelles trés mince de Teflon, avec un épaisseur de 0,05 à 0,1 mm. Les échantillons ont été irradiés dans le vide, jusqu'à 10^{-5} et avec beaucoup des lavages avec helium. Après ça les lamelles ont été mises à contact avec le monomère et, toujours dans le vide, laissées beaucoup de temps à $-25°C$. La polymèrisation a été conduite à trois temperatures: 25°, 40°, 82°, toujours dans le vide, pour des temps differents; puis on a separé le monomère et determiné les courbes cinetiques de greffage.

Les points marqués sur la figure indiquent les valeurs expérimentaux que nous avons trouvé. Les trois courbes ont été tracées en employant la rélation que vous pouvez



Discussion Figure 1.

lire sur le diagramme. Les valeurs Q_t et Q_∞ sont les quantités graffées au temps t et au temps infini, que nous appelerons temps de saturation.

Pour atteindre cette saturation vous voyez qu'il faut presque 90 heures à 25°, 35h à 40° et 10h à 82°.

La courbe est logaritmique et depend comme on voit d'une seule constante k_1. Nous avons cherché d'expliquer cette chose avec des mécanismes cinetiques (qui serait impossible de reporter ici), en supposant que les quantités greffées soient proportionelles aux radicaux, qui ont réagit au temps t et au temps de saturation.

Des considerations sur la relation écrite et sur la constante k_1 peut justifier cette hypothèse.

Comme on voit, les courbes ont la même allure d'une reaction de 1er ordre, mais l'interprétation de la constante k_1, n'est pas facile et immediate.

Elle peut dépendre de la diffusion du monomère, de l'activation des molécules de styrène qui doivent réagir, ou enfin être liée à la destruction du réseau cristallin du Teflon. Nous pouvons penser que l'énergie d'activation et celle de destruction restent constantes pendent tout le temps de greffage, tandis que la diffusion dévrait changer, car pendent le greffage change la structure du polymère.

Le fait que la k_1 reste constant pendent tout le temps, aussi pour une transformation presque totale, peut faire penser que la reaction soit essentiellement reglée par l'activation des molécules et par la destruction du réseau cristallin.

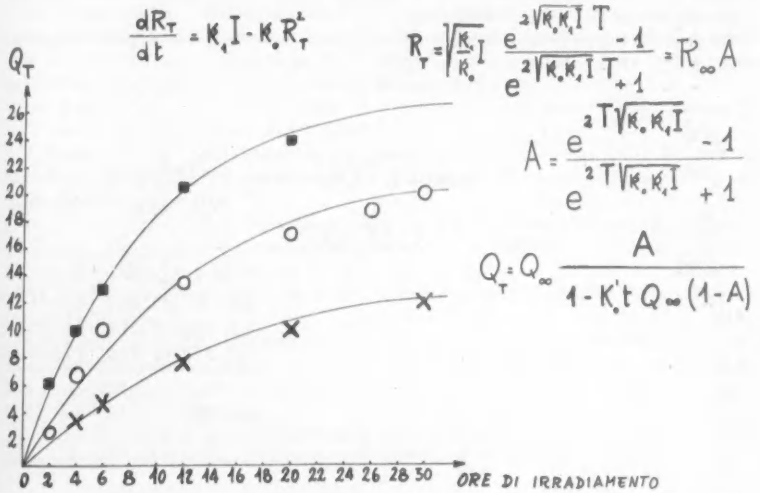
La constance de la k_1 encourage aussi l'hypothèse que les quantités greffées soient proportionelles aux radicaux car, si ça n'était pas vrai, la k_1 devrait, presque certainement, changer.

La possibilité que la variation de proportionalité et la variation de vitesse de diffusion peuvent se compenser pour donner une k_1 exactement constante pendent le temps, nous semble peu probable, quoique possible; la chose devra par consequence etre encore étudiée et éclaircie.

Nous avons trouvé une chaleur d'activation environ de 9000 calories, qui selon nous ne devrait pas être attribuée à la diffusion, mais à l'activation des molécules du monomère et surtout à la destruction du réseau cristallin.

Nos recherches actuelles sont orientées pour chercher d'expliquer quel rapport ce passe entre les differents hypothese.

Nous avons fait aussi des mésures sur des même lamelles de Teflon mais irradiées pour des temps croissants et, après, greffées jusqu'à saturation. Si nous faisons encore la supposition que la quantité greffée est toujours proportionelle aux radicaux qui sont presents au commencement, les courbes qui nous donnent la quantité greffée en fonction du temps d'irradiation, peuvent etre interprétées comme les courbes cinetiques de formation des radicaux. En effet la chose est un peu plus compliquée, parce qu'il faut tenir compt de la recombinaison spontanée des radicaux, qui fait abaisser leur concentration pendent le greffage. Il est possible de faire ce calcule mais nous n'avons pas ici la possibilité de faire une exposition complete par consequence, nous nous limiterons seulement à vous montrer les conclusions.


$\frac{dR_T}{dt} = K_1 I - K_0 R_T^2$
$R_T = \sqrt{\frac{K_1}{K_0}} I \frac{e^{2\sqrt{K_0 K_1 I}\, T} - 1}{e^{2\sqrt{K_0 K_1 I}\, T} + 1} = R_\infty A$
$A = \frac{e^{2T\sqrt{K_0 K_1 I}} - 1}{e^{2T\sqrt{K_0 K_1 I}} + 1}$
$Q_T = Q_\infty \frac{A}{1 - K_0' t\, Q_\infty (1 - A)}$
Q_T
26
24
22
20
18
16
14
12
10
8
6
4
2
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
ORE DI IRRADIAMENTO

Discussion Figure 2.

Dans le diagramme vous voyez trois courbes qui se réfèrent à trois températures differentes de greffage; sur les abscisses sont réportés les temps d'irradiation et sur les ordonnées les quantitées greffées de saturation, c'est à dire, après un temps très grand de polymérisation, qui nous avons trouvé etre de 90^h à 25°, de 35^h à 40°, et de 10^h à 82°C.

Les points ont été obtenus expérimentellement, tandis que les courbes ont été calculées en supposant une vitesse de formation des radicaux

$$\frac{dR_T}{dt} = K_1 I - K_0 R_T^2$$

Si on resoudre cette differentielle, on arrive à une rélation que nous donne les radicaux formés au temps d'irradiation T.

$$R_T = \sqrt{\frac{K_1}{K_0}}\, I\, \frac{e^{2\sqrt{K_1 K_0 I}\, T} - 1}{e^{2\sqrt{K_1 K_0 I}\, T} + 2} = \sqrt{\frac{K_1}{K_0}}\, I\, A$$

ou:

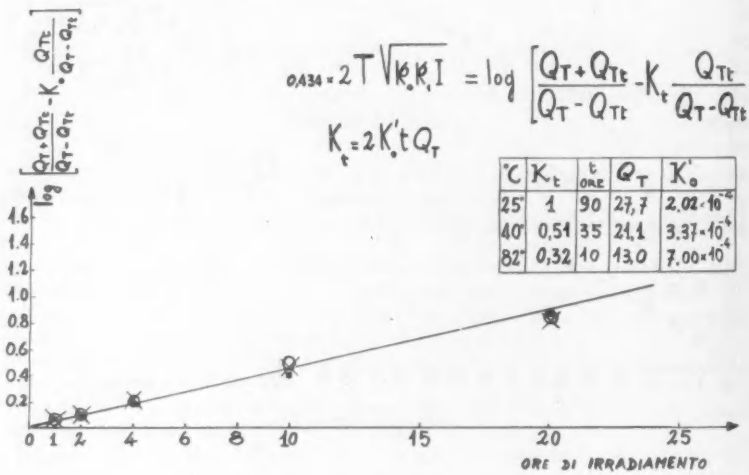
$$A = \frac{l^{2T\sqrt{K_1K_0I}}\,T - 1}{l^{2T\sqrt{K_1K_2I}}\,T + 1}$$

De cette rélation corrigée, pour ce que nous avons dit sur la récombinaison spontanée des radicaux, nous arrivons à l'expression:

$$Q_t = Q_\infty \frac{A}{1 - K_0' t\, Q_\infty (1 - A)}$$

où la fonction A depend seulement des constantes cinetiques de formation des radicaux et doit être la même pour les trois courbes, t est le temps de saturation du greffage, temps qui est très long auxbas temperatures, et Q_∞ la quantité qui est greffée à l'équilibre après des temps très long d'irradiation.

On peut convalider cette rélation si on resoudre la même expression, pour l'exponentielle de A. On arrive ainsi à cette rélation:



Discussion Figure 3.

$$2T\sqrt{K_1K_0I} = 2{,}4 \log \left[\frac{Q_\infty + Q_{Tt}}{Q_\infty + Q_{Tt}} - K\frac{Q_{Tt}}{Q_\infty - Q_{Tt}}\right]$$

$$K = 2K_0 t Q_\infty$$

On voit que le logarithme n'est pas seulement une fonction rectiligne du temps d'irradiation T, mais que la droite doit être independente de la température de greffage.

En effet les points des trois courbes aux differents temps d'irradiation, se superposent assez bien et sont aussi assez bien allignées sur une droite.

Si on rémarque que les courbes calculées, ont été obtenues en faisant l'hypothèse d'un mécanisme cinetique très simple et raisonable, et en supposant seulement une proportionnalité entre les radicaux et la quantité greffée, la bonne concordance avec les points expérimentaux peut conforter notre supposition, qui s'accorde d'autre part avec ce que nous avons déjà dit à propos de la vitesse de greffage.

Le mécanisme que nous avons proposé sensible, peut être, trop simple pour un fenomène qui est consideré, en genèral très compliqué; mais il faut remarquer que nous cherché de simplifiere les plus possible les experiences. Nous avons travaillé avec des lamelle trés mince, avec un greffage esclusivement radicaleur, et une tecnique très prècise. Toutefois nous savons que le probleme reste toujour ouvert et il foudra encore d'autres contributions experimentaux pur l'éclaircie.

J. Dobó: It was shown by ESR measurements of Mrs. R. Marx, that in the dose range used by Prof. Rossi the concentration of free radicals is proportional to the applied dose. On the other hand, the recombination of radicals in the Teflon is very slow at the temperatures used. It follows that the relation between the applied dose and the total amount of grafting should perhaps be better described by abandoning the supposition that the length of the grafted chains is independent of the radical concentration.

P. Lebel (*Kléber-Colombes, Paris, France*): Je voudrais savoir, (au sujet des observations des auteurs sur l'effet de la température sur le greffage sous irradiation), si l'étude a été poursuivie à des temperatures assez élevées. En effet, nous avons observé qu'au dessus de 150°C, le styrolène se greffe sur le Teflon sans aucune autre activation que la chaleur (il n'y a dans ce cas ni radiation, ni catalyseur d'aucune sorte).

Le styrolène qui se polymérise dans ce cas se polymérise dans le Teflon sans qu'il soit possible de l'extraire par aucun solvant.

J. Dobó: We did not perform such experiments, but it is known from the work of Odian and others, that one can obtain by peroxide initiators products which behave like true graft copolymers.

W. K. W. Chen (*A.M.F., Springdale, Conn.*): We have also observed that styrene grafts onto Teflon films without any irradiation. In a few weeks, significant grafting occurs even at room temperature.

We have further observed that the rate of grafting is strongly affected by the structure of the Teflon film.

A. Chapiro (*C.N.R.S., Bellevue, France*): Nous avons également trouvé que des films de Teflon scellés sous vide avec du styrène gonflent au bout de quelques semaines à la température ordinaire et l'on obtient ainsi des produits tout à fait semblables aux films "greffés" par irradiation.

J. Dobó: We have obtained some differences with different films, but these did not influence significantly the constants determined.

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Comparison of Radiation- and Peroxide-Initiated Grafting of Styrene to Polyethylene Film

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I. INTRODUCTION

Graft copolymerization of vinyl monomers to a polymeric backbone has been achieved by many methods, most of them involving free-radical initiators. Field et al. prepared, probably, the first graft copolymer in 1930,[1] when they thermally polymerized styrene in rubber and mechanically masticated the resulting product. Shortly thereafter, organic peroxides were used for self-grafting of styrene onto polystyrene.[2] Radiation by far ultraviolet light was also introduced in this period.[3] At that time, the concept "graft copolymer" had not been introduced.

After the war, deliberate grafting by way of chain transfer mechanisms[4] was initiated by means of peroxides.[5] Significant interest in grafting reactions, however, did not develop until the general availability of high energy radiation.[6-11] These developments have been organized and discussed by Chapiro.[6] In most of these early studies of grafting induced by radiation, the weight gain after extensive washing (and drying) was used as the measure of apparent grafting, leaving open the question of the relative amounts of true covalent grafting and merely entrapped homopolymer (polymeric alloy). One of the purposes of this work is to provide a partial answer to the above question, since it is of both theoretical and practical interest.

Another aspect of this work is to compare the grafting results using initiation by high energy radiation with those obtained using an organic peroxide, and with those employing a combination of both.

A third purpose of this work is to report additional results which may assist in the understanding of the linear weight gain versus time relationship reported previously in the literature.[6-11]

The grafting systems employed in this investigation may be generally described as follows: (*A*) direct grafting (simultaneous gamma radiation and in-source grafting at room temperature); (*B*) post-radiation grafting (beta radiation in air followed by grafting in pure monomer at 65°C.); (*C*) post-radiation grafting with added peroxide (beta radiation in air followed by grafting in monomer containing various amounts of benzoyl peroxide at 65°C.); (*D*) chemical grafting (grafting by monomer containing low to moderate amounts of benzoyl peroxide at 65°C.).

One important factor in all four systems is that the integrity of the starting polymeric film was maintained by avoiding reaction temperatures high enough to dissolve the substrate. A different situation obtains if polyethylene is dissolved in styrene at a higher temperature than employed here. Our results are not the same as those reported for the homogeneous system at 80°C. reported by Potts et al.[12] The explanation for the discrepancy presumably resides in the difference between our heterogeneous and their homogeneous system.

II. EXPERIMENTAL

A. Direct Grafting by Gamma Rays

Commercial-grade styrene was washed with 20% sodium hydroxide solution followed by distilled water to remove the inhibitor. It was dried over anhydrous sodium sulfate and distilled at 18 mm. Hg under nitrogen. Samples of polyethylene film of known weight in Pyrex ampules (1 × 12 in.) were allowed to swell in a large excess of styrene at room temperature. The ampules were then evacuated and sealed at a vacuum of 10^{-3}–10^{-4} mm. Hg by the standard freezing and thawing procedure. The swollen samples were irradiated at ambient temperature with two different sources of Co^{60} gamma rays of nearly the same intensity: a 172,000 rep/hr. source at the Brookhaven National Laboratory, or a 165,000 rep/hr. source at Columbia University. The ampules were opened and the film washed with solvent within 30 min. after radiation. The increase in weight of the film was determined after washing in benzene until no polystyrene was detectable in the washing by precipitation in methanol, and drying for 18 hr. at 50°C. in a vacuum of 1–3 mm. Hg.

Two types of experiments were conducted in this manner. In one group, polyethylene films made from antioxidant-free resin of 0.914 g./cm.^{3} density and 26,000 molecular weight in three different thicknesses (1.5, 4, and 10 mil; 40 mil = 1 mm.) were directly grafted for various irradiation times. One set of samples comprising films of all three thicknesses was rolled into a single roll and directly grafted in the same ampule for 4.7 hr. to minimize ambient differences. In a second series, three films of different densities but of approximately the same thickness (0.914 g./cm.^{3}, 4 mils; 0.934, g./cm.^{3}, 5 mils; 0.95 g./cm.^{3}, 5 mils) were directly grafted in the same ampule to a total dose of 1.35 Mrep.

B. Post-Radiation Grafting by Beta Rays

A 2-M.e.v. resonance transformer provided by the X-ray Division of the General Electric Co., Milwaukee, Wisconsin was used to irradiate, in air, 5-mil polyethylene film of 0.934 g./cm.^{3} density (Visking Co.) with doses ranging from 15 to 100 Mrad. The dosimetry was monitored colorimetrically with cellophane film containing a blue azo dye (duPont).[13] Many passes were used to minimize heating effects.

Irradiated films were allowed to "cool" for at least one week. Weighed samples of 5 cm. × 5 cm. were placed in excess styrene at 65°C. and withdrawn after 1, 2, 3.5, 5, and 7 hr., washed three times for 30 min. each with copious amounts of toluene, and dried to constant weight at 45°C.

C. Post-Radiation Grafting with Added Peroxide

The procedure was the same as in method B, except the post-irradiation reaction was carried out in excess styrene monomer at 65°C. containing various amounts of benzoyl peroxide. This is to compare the peroxide contribution to the rate of apparent grafting.

D. Chemical Grafting Initiated by Benzoyl Peroxide

Polyethylene films of 0.93 g./cm.^{3} density were placed in excess styrene at 65°C. containing various amounts of benzoyl peroxide. After various lengths of time they were withdrawn, washed, and dried in the same manner as described above.

E. Fractionation of the Apparent Graft Copolymers

Each sample was dissolved in toluene at 90°, and fractionated as a 1% solution by precipitation with methanol at various γ values, when

$$\gamma = \frac{\text{ml. methanol added}}{\text{ml. toluene} + \text{ml. methanol added}} \times 100$$

If a fraction precipitated merely by slow cooling (150 min. to room temperature) without addition of methanol, γ is taken as zero. In the case of samples obtained from post-radiation grafting after beta ray treatment, there was an initial fraction insoluble in hot toluene. Each precipitated fraction was separated by centrifugation (30,000 rpm) and dried at 75°C. under 1–3 mm. Hg. Each fraction was characterized by carbon-hydrogen microanalysis.

F. Viscometric Molecular Weight of Polystyrene Fractions

Some of the samples fractionated by procedure E were essentially pure polystyrene, they were dissolved in benzene, and their intrinsic viscosities were obtained in a Cannon-Fenske viscometer in 0.1–2.0% solutions at 30°C. The Ewart-Tingey constants[14] for polystyrene at 30°C. were used to calculate molecular weight:

$$[\eta] = 0.97 \times 10^{-4} M^{0.74}$$

III. RESULTS

A. Direct Grafting by Gamma Rays

The rate of apparent grafting $[(W - W_0)/W_0]$ versus time of styrene to polyethylene films of various thicknesses was plotted on a log-log scale

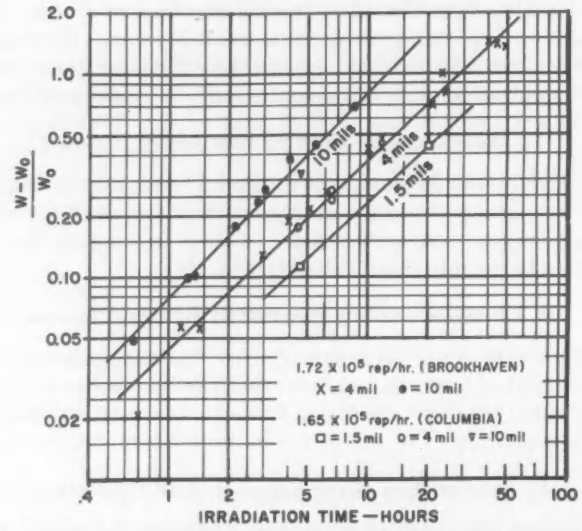

Fig. 1. Direct grafting of styrene to polyethylene films. Film density 0.91, temperature 25°C.

in Figure 1. The parallel straight lines with slopes of unity again confirm the linear time dependency. A set of similar results published earlier[8] was included in this new form of plotting to show the reproducibility. There is little doubt that the thicker the film, the faster the rate of apparent grafting. The relative rate is 3.2:1.6:1 for 10 mil, 4 mil, and 1.5 mil films, respectively. Furthermore, this ratio is maintained over a wide range, at least tenfold. The set grafted simultaneously for 4.7 hr. also conforms to this pattern. These results do not support the view that thicker films graft slower due to slower monomer diffusion into the film.

The effect of polyethylene film density on the rate of apparent grafting is given in Table I. Here again diffusion is not rate-controlling—the higher density film grafts faster although the diffusion of monomer is

TABLE I
Effect of Density of Polyethylene Film on Its Apparent Grafting with Styrene[a]

Density of film, g./cm.³	Thickness of film, mil	Equilibrium swelling in monomer (25°C.), %	Apparent graft $\left(\frac{W - W_0}{W_0}\right)$
0.914	4	12[b]	0.37
0.934	5	6[c]	0.75
0.95	5	5[c]	0.80

[a] Dose rate = 1.72×10^5 rep/hr.; total dose = 1.35×10^6 rep.
[b] Data of Chen.[15]
[c] Data of Frillici.[16]

slower. These samples were run at the same time in the same ampule. If monomer concentration within the swollen film were rate-determining, then the lower crystallinity film with higher monomer swelling ratio would graft faster. The answer must be sought elsewhere.

B. Post-Radiation Grafting

The rate of apparent grafting after exposure to beta rays is shown in the lower curves of Figures 2–5. The characteristic linear rate of apparent grafting with time develops after an induction period. Consistent linearity is enhanced by remembering that during this initial hour up to 5% of the polyethylene is extracted,[11] thereby diminishing the net result at the begin-

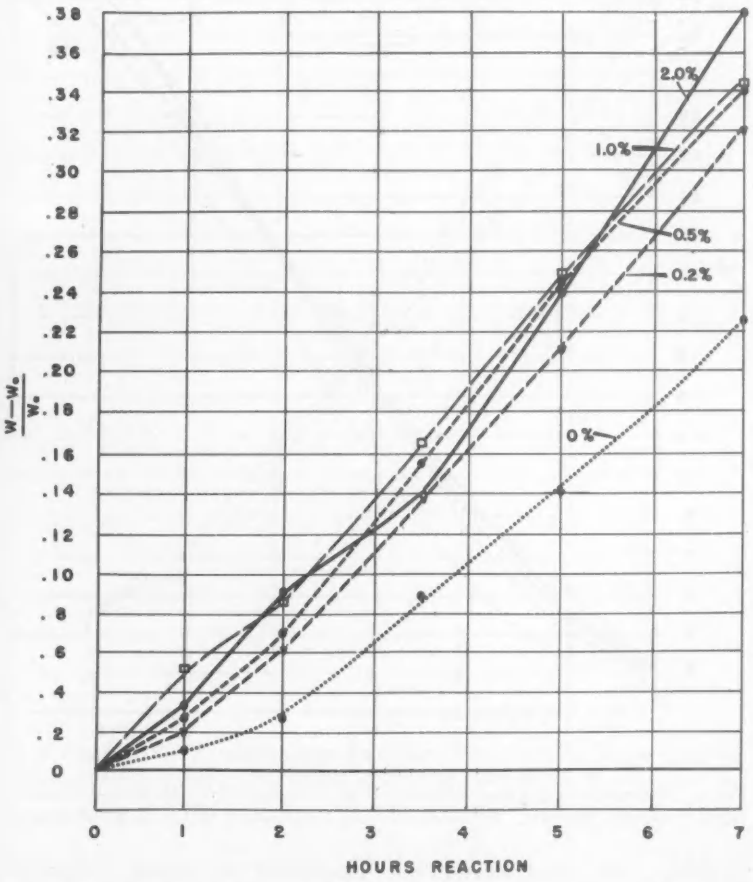

Fig. 2. Post-radiation grafting of styrene to polyethylene film with various concentrations of benzoyl peroxide. Film density 0.93, temperature 65°C., 15 Mrad beta ray.

ning. The small amount of thermal grafting without radiation or peroxide is shown by the bottom curve in Figure 6.

As to dosage, pre-irradiation up to 15 Mrad enhances the rate of apparent grafting, but doses from 35 Mrad up to 100 Mrad give no further

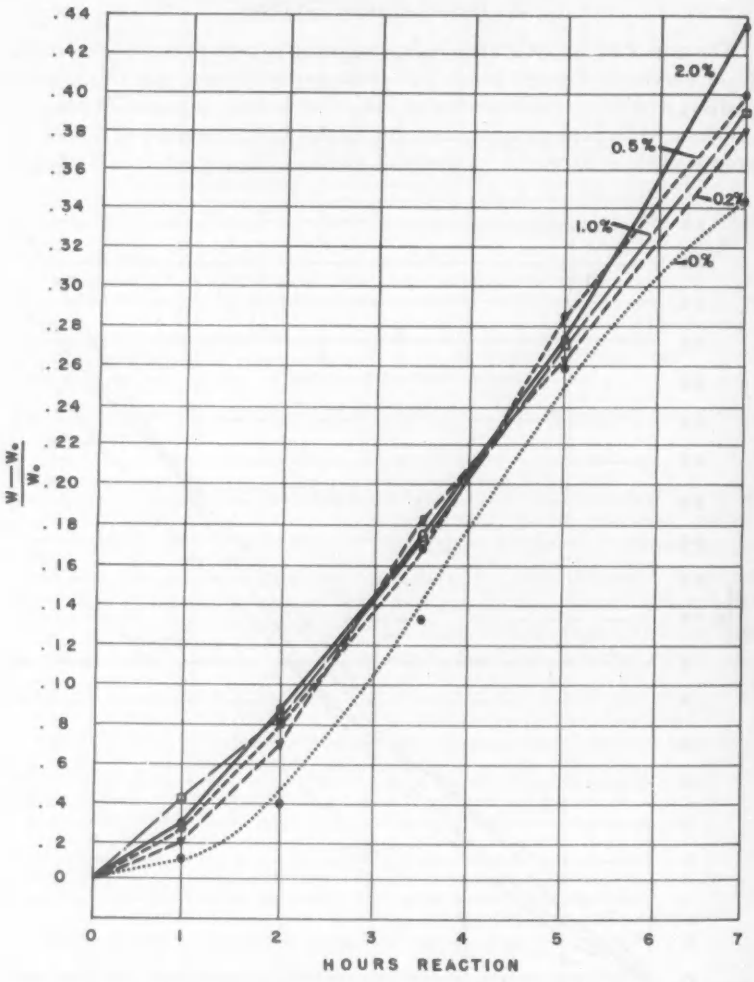

Fig. 3. Post-radiation grafting of styrene to polyethylene film with various concentrations of benzoyl peroxide. Film density 0.93, temperature 65°C., 35 Mrad beta ray.

increase. The usual square root dependence on initiator, applicable only to systems with bimolecular termination, is definitely not followed here.

C. Post-Radiation Grafting with Added Peroxide

The upper lines in Figures 2–5 show the rate of apparent grafting after exposure to beta rays supplemented by various amounts of benzoyl per-

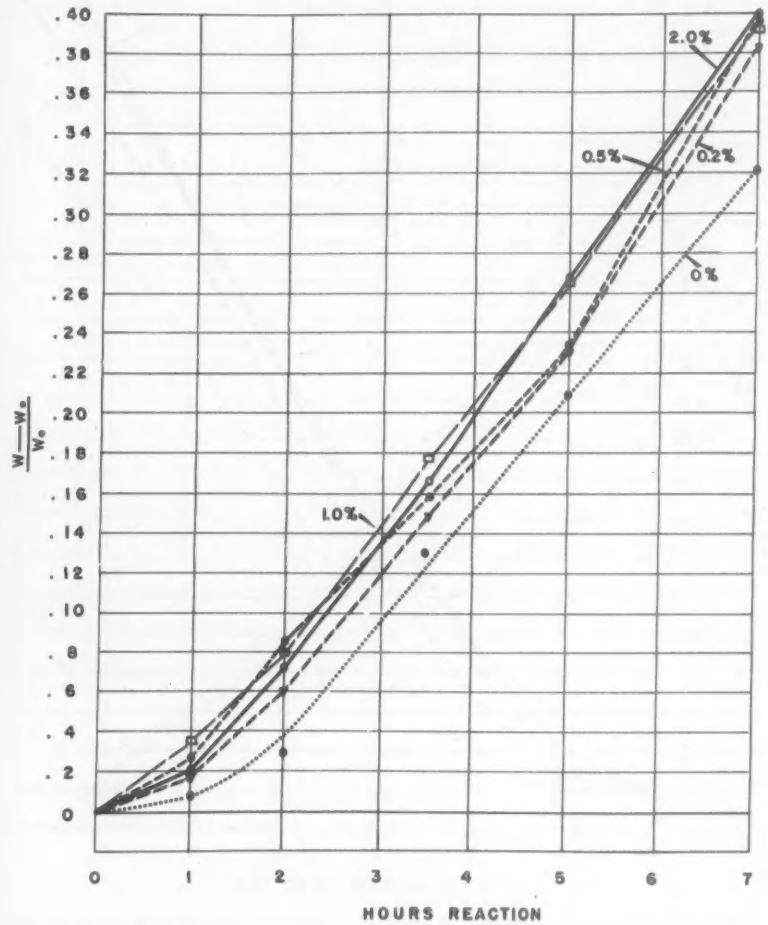

Fig. 4. Post-radiation grafting of styrene to polyethylene film with various concentrations of benzoyl peroxide. Film density 0.93, temperature 65°C., 65 Mrad beta ray.

oxide. The linear relationship with time is again observed. Just as experienced for higher dosage, added peroxide appears to have little effect on the rate for the range studied.

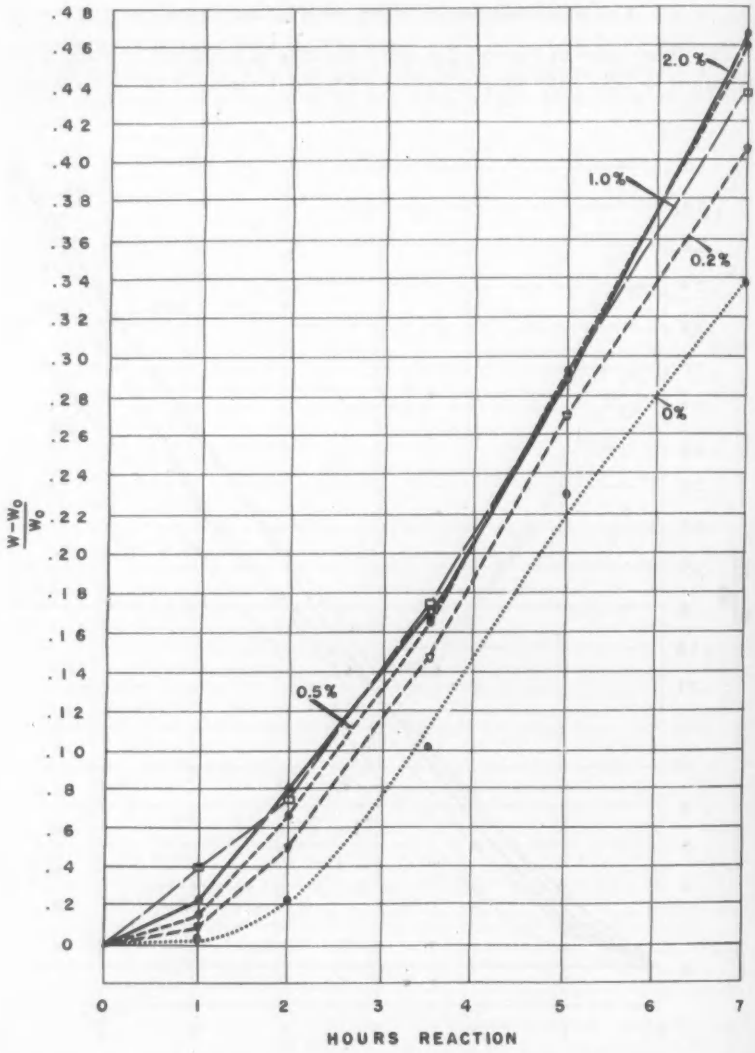

Fig. 5. Post-radiation grafting of styrene to polyethylene film with various concentrations of benzoyl peroxide. Film density 0.93, temperature 65°C., 100 Mrad beta ray.

D. Chemical Grafting Initiated by Benzoyl Peroxide

Figure 6 shows the rate of apparent grafting initiated by seven concentrations of benzoyl peroxide alone. Within the range employed (0–2%) added peroxide increases the rate of reaction monotonically.

E. Determination of the Extent of Covalent Grafting

The results on fractionation of some of the apparently grafted films prepared by methods A, C, and D are summarized in Table II. In addition, Table III shows a comparison between molecular weights of polystyrene formed (a) in contact with the swollen film, (b) in the absence of

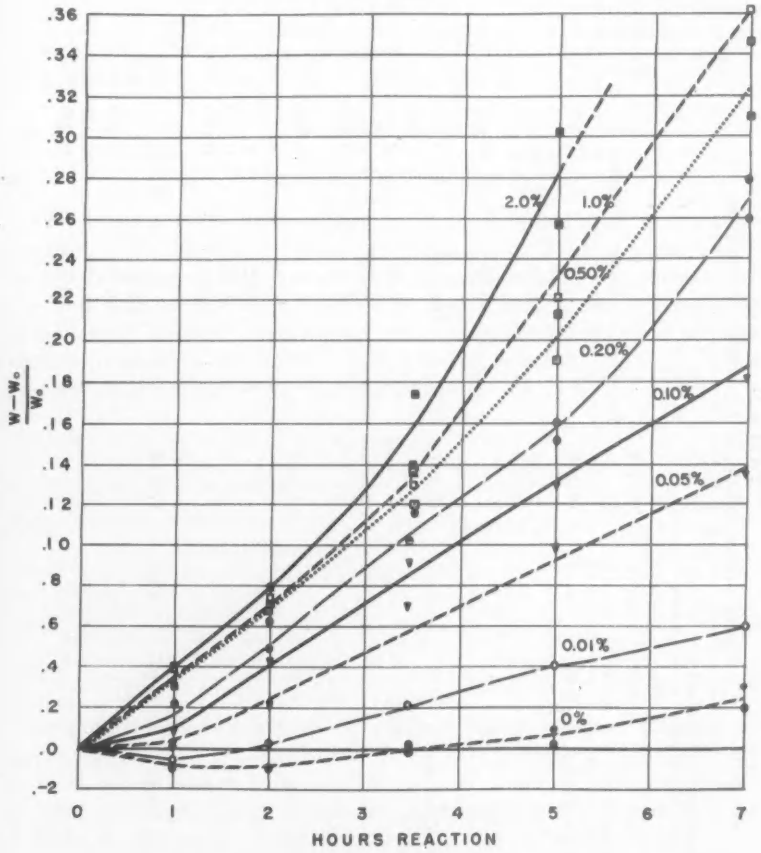

Fig. 6. Chemical grafting of styrene to polyethylene films initiated by various concentrations of benzoyl peroxide. Film density 0.93, temperature 65°C., no radiation.

film, and (c) within the swollen film. The homopolymer obtained from the fractionation of the direct graft has a molecular weight four times that of the control, indicating a substantial reduction in the termination inside the swollen film.

TABLE II
Results on Fractionation of Apparently Grafted Film

No.	Description of grafted film: Grafting method	Film density, g./cm.³	Apparent graft level, %	Sample wt., g.	Fraction	γ Value	Fraction wt., g.	Recovery, %	Analysis: PE, %	Pst, %	Mol. wt.
I	Method D (0.2% Bz_2O_2)	0.93	21.5	9.976	1	0	7.783		92	8	—
					2	0–20	0		—	—	—
					3	20–25	0.261		—	97	[a]
					4	25–29	0.620		—	96	[a]
					5	30–39	0.466		—	96	530,000
								91.6			
II	Method C (15 Mrad beta + 0.2% Bz_2O_2)	0.93	23.5	10.007	1	Insoluble	8.250		69	31	—
					2	0	1.419		97	—	—
					3	0–20	0				—
					4	20–29	0				—
					5	30–40	0.062		92	—	—
								97.3			
III A	Method A (1.35 Mrep gamma)	0.91	27.1	10.251	1	0	8.618		81	19	—
					2	0–20	0		—	—	—
					3	20–29	1.249		—	97	224,000
					4	30–39	0.206		—	93	50,100
					5	40–60	0.035		—	100	—
								98.6			
III B	Method A (2.70 Mrep gamma)	0.91	45.8	17.313	1	0	14,932		61	39	
					2	0–20	0		—	—	
					3	20–29	0.999		—	99	263,000
					4	30–39	0.198		—	93	56,200
					5	40–50	0.050		—	100	—
								93.4			

[a] Not determined.

TABLE III
Comparison of Molecular Weights of Polystyrene in Ambient Liquid and in Film Phase

No.[a]	Description	Radiation dose, Mrep[b]	Molecular weight
III A	Polystyrene formed in contact with	1.35	79,500
III B	swollen film, direct grafting	2.70	83,000
	Polystyrene, control, no film present	1.35	47,900
III B	Polystyrene homopolymer from the film phase	2.70	178,000

[a] Refers to experiment numbers in Table II.
[b] Co^{60} source; dose rate = 1.72×10^5 rep/hr.

IV. DISCUSSION

A. Extent of Covalent Grafting

The results in Table II can be used to calculate the extent of true covalent grafting. The fraction collected at γ values of 20–40 are essentially homopolymers of styrene not bonded to polyethylene. Polystyrene in the insoluble fractions or those collected at zero γ values can be considered as covalently grafted; their weight, divided by the total weight of polystyrene present can be taken as the extent of covalent grafting. Table IV gives these values for grafting methods A, C, and D.

TABLE IV
Extent of Covalent Grafting by Various Methods

Grafting method	Apparent graft level, %	Extent of covalent grafting, %
Method D (0.2% Bz_2O_2)	21.5	32
Method A (1.35 Mrep gamma)	27.1	53
Method A (2.7 Mrep gamma)	45.8	83
Method C (15 Mrad beta + 0.2% Bz_2O_2)	23.5	98

Although method B with beta radiation alone, was not included in this study, it is fair to assume that the extent of covalent grafting would be high, and comparable to that of method C (98%). The extent of covalent grafting is lowest for method D, although it may vary somewhat with the benzoyl peroxide concentration, as indicated by Potts et al.[12]

B. Rate of Apparent Grafting

The direct grafting rate has been shown to be independent of dose rate in the range of 0.065 Mrep/hr. to 0.30 Mrep/hr. with only a slight decrease at 0.020 Mrep/hr.[3] The results in Figures 2–5 also show a lack of significant dependency of grafting rate on the pre-irradiation dosage and added peroxide concentration. In order to see this more clearly, the apparent graft levels in Figures 2–6 for the 5-hr. points are plotted versus per cent

benzoyl peroxide in Figure 7. The values converge towards 0.25 ± 0.04, when 35–100 Mrad pre-irradiation, 15 Mrad plus 0.2% benzoyl peroxide, or 1–2% benzoyl peroxide were employed to initiate the polymerization. Such a limiting value suggests that an equilibrium level of growing chains has been reached; polymerization rate is constant, which is supported by the observed linear time dependence. The equilibrium concentration of growing chains may be a function of the crystallinity and other morphological characteristics of the polyethylene substrate.

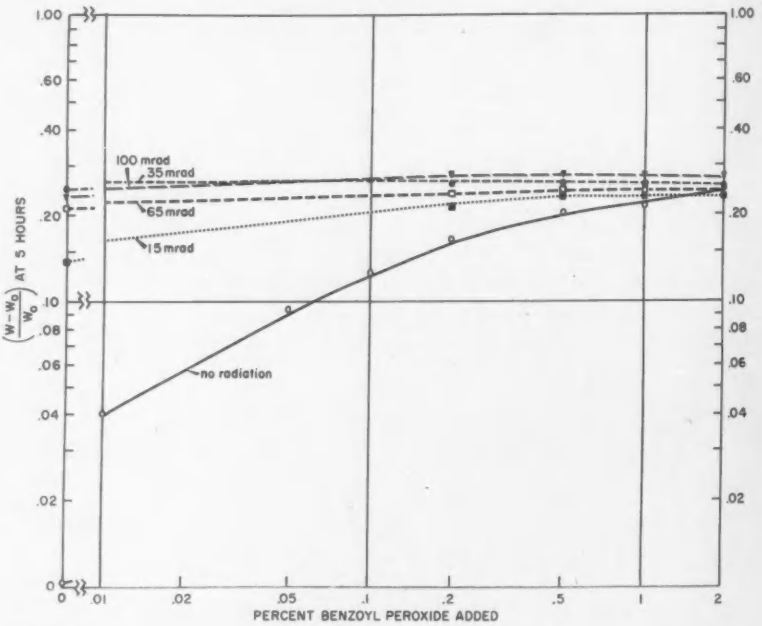

Fig. 7. Apparent graft level after 5 hr. plotted against concentration of added benzoyl peroxide: (▼) 100 Mrad, (□) 65 Mrad, (●) 35 Mrad, (■) 15 Mrad, (○) no radiation.

The heterogeneous systems studied in this investigation, namely, regions of amorphous polyethylene swollen with styrene, dispersed among regions of crystalline polyethylene, bear much resemblance to emulsion polymerization.[18]

Molecular weight of polystyrene formed within the substrate is higher than that formed in the bulk styrene, when subjected to the same initiation.

Overall polymerization rate is relatively independent of initiation rate, (except when the initiator concentration is below a certain level). In emulsion polymerization systems, the rate is proportional to the number of micelles.

The swollen amphorous regions have approximately the same size range as growing micelles in emulsion systems. This was shown by Goldring,[19] who deposited silver shadows in the polyelectrolyte regions of ion-exchange membranes made from polyethylene–polystyrene graft polymer films.[20] His electron microscope studies showed these regions to be several hundred Angstroms in diameter.

C. Effect of Film Thickness and Density

The faster grafting rate with thicker and higher density film shown in Figure 1 and Table I contradicts the view that slower monomer diffusion into the film reduces the rate for thicker films. The Trommsdorff effect may account for the higher molecular weight of homopolymeric polystyrene formed within the swollen film. It may be postulated that the slightly higher density in the center layer of thicker films, coupled with higher gel viscosity caused by the lower monomer concentration, increases the Trommsdorff effect sufficiently to cause a net rise in polymerization rate. This postulation, however, does not adequately explain the 3.2:1.6:1.0 increase in rate shown in Table I. Here the density and monomer concentration differences between the film materials are more pronounced than can be expected from thickness variation alone.

An alternative is to consider the discussion in the previous section regarding emulsion polymerization type kinetics and to postulate that the number of swollen amorphous polyethylene "micelles" is higher in films of higher density and thickness thus accounting for their higher rate of apparent grafting. This view, however, needs to be supported by more data and a better understanding of the morphology of the films studied.

It is a pleasure to acknowledge the experimental assistance of Messrs. H. Halter and C. A. Wetmore and Miss B. L. Alexanders.

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Synopsis

Polyethylene films were modified by "grafting" with styrene by the following means: (A) gamma-irradiation from Co^{60} with film immersed in liquid monomer; (B) beta-irradiation in air followed by contact with liquid monomer; (C) treatment with liquid monomer containing benzoyl peroxide. The rates of polymerization, the degree of actual covalent grafting, and mechanical properties are discussed with regard to crystallinity of the starting film, the level of grafting and initiation rate. It was found that the amount of actual covalent bonding determined by fractional precipitation was the least by method (C) and the most by method (B). Methods (A) and (C) yield products soluble in hot xylene. It was also found that homopolymeric styrene separated from the interior of the grafted film has a considerably higher molecular weight than that formed in the surrounding bath (Trommsdorff effect). Films of low crystallinity (density = 0.91 g./cm.^{3}) showed a high level of microheterogeneity when prepared by method (C). This phenomenon did not occur with films of higher crystallinity (density = 0.93–0.96 g./cm.^{3}). It is shown that this effect is related to the diffusion of oxygen into the film. The amount of grafting is shown to be relatively independent of the level of preirradiation in the range of 10–20 Mrad.

Résumé

Des films de polyéthylène ont été modifiée par greffage avec du styrène au moyen des méthodes suivantes: (A) Irradiation gamma au moyen de Cobalt 60 avec le film immergé dans le monomère liquide; (B) Irradiation-bêta dans l'air, suivi du contact avec le monomère liquide; (C) Traitement avec le monomère liquide contenant du peroxyde de benzoyle. Les vitesses de polymérisation, le degré de greffage covalent réel et les propriétés mécaniques sont discutées du point de vue de la cristallinité du film de départ, du niveau de "greffage" et de la vitesse d'initiation. On a trouvé que la teneur en liaison covalente réelle déterminée par précipitation fractionnée était la plus faible par la méthode (C) et la plus élevée par la méthode (B). Les méthodes (A) et (C) fournissent des produits solubles dans le xylène à chaud. On a également trouvé que le styrène homopolymère séparé de l'intérieur du film greffé avait un poids moléculaire considérablement plus élevé que celui formé dans le mélange réactionnel environnant (Effet Trommsdorff). Les films de faible cristallinité (densité = 0.91 g/cm.^{3}) présentent un niveau élevé de microhétérogénéité lorsqu'ils sont préparés par la méthode (C). Ce phénomène n'a pas lieu avec les films de cristallinité plus élevée (densité = 0.93–0.96 g./cm.^{3}). On montre que cet effet est relié à la diffusion d'oxygène dans le film. On montre que la quantité de "greffage" est relativement indépendante du niveau de préirradiation dans le domaine de 10–20 mégarads.

Zusammenfassung

Polyäthylenfilme wurden durch Aufpfropfung von Styrol nach folgenden Methoden modifiziert: (A) γ-Strahlung von Cobalt-60 auf den in flüssiges Monomeres getauchten

Film. (A) β-Bestrahlung in Luft und darauffolgender Kontakt mit flüssigem Monomeren. (C) Behandlung mit Benzoylperoxyd-hältigem flüssigen Monomerem. Die Polymerisationsgeschwindigkeit, der Grad der tatsächlichen covalenten Aufpfropfung und die mechanischen Eigenschaften werden in Hinblick auf die Kristallinität des ursprünglichen Filmes, die Höhe der Pfropfung und der Startgeschwindigkeit diskutiert. Der Betrag der aktuellen covalenten Bindung wurde durch fraktionierte Fällung bestimmt und war bei Methode (C) am geringsten und bei Methode (B) am grössten. Methode (A) und (C) liefern in heissem Xylol lösliche Produkte. Das aus dem Inneren des gepfropften Filmes isolierte Homopolystyrol besass ein beträchtlich höheres Molekulargewicht als das in der umgebenden Flüssigkeit gebildete (Trommsdorf-Effekt). Filme mit niedriger Kristallinität (Dichte = 0,91 g/cm³) zeigten bei Darstellung nach Methode (C) stark ausgeprägte Mikroheterogenität. Diese Erscheinung trat bei Filmen mit hoher Kristallinität (Dichte = 0,93–0,96 g/cm³) nicht auf. Dieser Effekt steht in Beziehung zur Diffusion von Sauerstoff in den Film. Der Betrag der Aufpfropfung ist im Bereich von 10–20 Megarad von der Höhe der Vorbestrahlung verhältnismässig unabhängig.

Discussion

J. Dobó (*Institut de Recherches des Matières Plastiques, Budapest, Hungary*): We performed with T. Czvikovsky similar fractionation experiments on the polyethylene–styrene grafts, which were mentioned in this Symposium (pp. 1173–1193). The main differences lie in the extent of covalent grafting, for which we obtained much lower values, in many cases even 0%. The differences may be caused in part by the fact, that we redissolved and reprecipitated our fractions, to avoid coprecipitation. On the other hand, when Dr. Chen irradiated polyethylene by 15 Mrad electrons, he received some crosslinked polyethylene and the polystyrene could be retained by intercrosslinking like in the systems described by Charlesby and Pinner (Industrie des Plastiques modernes....).

E. Selegny (*Faculté des Sciences, Nantes, France*): Je suis d'accord avec M. Dobo en ce qui concerne les probabilités de pontage à haute dose d'irradiation.

Je voudrais en outre savoir si les membranes décrites dans la communication d'hier du Dr. Friedlander étaient préparées par la méthode A, B, ou C? Que par conséquent les membranes étaient formées effectivement de polymères greffés ou étaient du type "snack-cage."

M. Lazar (*C.S.A.V., Bratislava, Czechoslovakia*): I would like to ask if you have investigated the extent of covalent grafting in a set of polyethylene films of various thicknesses. I think, from these data it would be possible to estimate if the higher rate of apparent grafting in the thicker film is due to a slower extraction of homopolystyrene by the monomeric styrene from the grafted polyethylene during the reaction.

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Greffage des Mélanges Styréne-Acrylonitrile sur le Poly(Chlorure de Vinyle) par la Méthode Radiochimique Directe

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I. INTRODUCTION

Plusieurs études ont déjà été publiées sur le greffage radiochimique d'un mélange de deux monomères sur un polymère. C'est ainsi que Odian et collaborateurs ont greffé des mélanges de styrène et d'acrylonitrile, de styrène et de 4-vinylpyridine et de styrène et d'acrylate de méthyle sur le polyéthylène[1] et le polytetrafluoroéthylène.[2] Chandler et collaborateurs[3] ont étudié le greffage des mélanges styrène–acrylonitrile sur le polyéthylène; Ide[4] a greffé un mélange d'acrylate de méthyle et d'acrylonitrile sur la cellulose; enfin Sakurada et collaborateurs[5] ont greffé un mélange de butadiène et de styrène sur ce même polymère.

Certains de ces auteurs[1,2] ont signalé que la composition des branches greffées était différente de celle du copolymère statistique obtenu par copolymérisation radicalaire, résultat difficile à comprendre dans le cadre de la cinétique des réactions radicalaires. Un des buts de notre travail était de vérifier si ce résultat n'était pas imputable à la différence des vitesses de diffusion des deux monomères dans le polymère à greffer. En effet, nos études antérieures avaient attiré notre attention sur l'importance des phénomènes de diffusion dans la plupart des réactions de greffage qui s'effectuent en milieu gel et nous avions trouvé en particulier[6] que la vitesse de diffusion dans un film de poly(chlorure de vinyle) était beaucoup plus grande pour le méthacrylate de méthyle que pour le styrène. Il en resultait que la vitesse de greffage à 20°C était entièrement contrôlée par la vitesse de diffusion du monomère dans le cas du styrène, tandis que dans le cas du méthacrylate de méthyle, la cinétique du greffage était "normale". Lorsque la température de la réaction était portée à 60°C, la diffusion était fortement accélérée et ce processus cessait de contrôler la cinétique du greffage même dans le cas du styrène.[7]

Dans le présent travail, nous décrirons nos resultats préliminaires obtenus au cours de l'étude du greffage des mélanges styrène-acrylonitrile sur des films de poly(chlorure de vinyle). Nous avons choisi ces deux monomères car ils diffusent avec des vitesses très différentes dans le poly(chlorure de

vinyle) (l'acrylonitrile diffusant beaucoup plus vite que le styrène). D'autre part, la présence d'azote dans l'acrylonitrile permet un dosage facile de la composition des copolymères formés.

Dans ce qui suit, nous presentons d'abord quelques résultats sur le gonflement du film de poly(chlorure de vinyle) dans les mélanges styrène–acrylonitrile, nous décrirons ensuite les résultats de l'étude cinétique du greffage et enfin quelques expériences sur la copolymérisation radiochimique de ces deux monomères.

II. CONDITIONS EXPERIMENTALES

A. Conduite des Expériences de Greffage

Nous avons utilisé des conditions expérimentales analogues à celles de nos expériences antérieures sur le greffage du styrène et du méthacrylate de méthyle sur films de poly(chlorure de vinyle).[6] Des feuillets d'un poids moyen de 0,15 g étaient découpés dans une feuille de Lucoflex de 0,35 mm d'épaisseur. Ces feuillets étaient ensuite scellés sous vide, dans des tubes de pyrex, avec 10 cm^3 du mélange des monomères. Toutes les irradiations ont été effectuées à 20°C avec les rayons γ du Cobalt-60. Les doses utilisées variaient de 2.016 à 40.320 rads. L'intensité était de 0,28 rads/sec. Ces conditions expérimentales ont été choisies de manière à réduire au minimum l'influence de la vitesse de diffusion des monomères sur la cinétique du greffage.[6]

Afin d'assurer le gonflement de chaque film de polymère avant l'irradiation, les tubes scellés renfermant le polymère et les monomères étaient stockés pendant au moins 10 heures à la température ordinaire avant chaque expérience.

Après l'irradiation, les films greffés étaient extraits des tubes, lavés dans le benzène pendant 48 heures, séchés et pesés.

B. Copolymérisation

Les vitesses de copolymérisation de différents mélanges de styrène et d'acrylonitrile ont été mesurées par dilatométrie dans des conditions d'irradiation identiques à celles des expériences de greffage. De plus, les quantités de copolymère formées au cours des expériences de greffage dans l'excès du mélange des monomères qui entourait les films, étaient déterminées par pesée. Les résultats de ces mesures étaient comparés aux résultats des mesures dilatométriques.

La composition des copolymères était déduite des microdosages de C, H et N. Pour les films greffés, la composition était calculée à partir des résultats des microdosages de C, H N et Cl.

C. Gonflement des Films de Polymère

Les mesures de gonflement ont été effectuées dans un thermostat à 22°C. Des films pesant de 0,1 à 0,2 g étaient plongés dans le monomère ou le

mélange de monomères examiné et le poids des films gonflés était détermine à intervalles de temps réguliers. Pour cela, chaque film, à sa sortie du bain des monomères, était rapidement pressé entre deux feuilles de papier filter, puis pesé dans un vase à tarer bouché.

La composition du mélange de monomères qui avait pénétré danslesé films a été déterminée de la façon suivante: un film de poly(chlorure de vinyle) était mis en contact avec un mélange bien déterminé et on mesurait la variation de la composition de ce mélange après 30 minutes de contact ainsi qu'à l'équilibre de gonflement. Les compositions des mélanges de monomères étaient déduites de leur indice de réfraction mesuré à 25°C. On avait auparavant établi la courbe d'étalonnage des indices en fonction de la composition des mélanges de styrène et d'acrylonitrile.

III. RESULTATS

A. Gonflement des Films de Poly(Chlorure de Vinyle) dans les Mélanges Styrène–Acrylonitrile

Ces expériences de gonflement ont été effectuées afin de connaitre la concentration réelle des monomères dans les films pour différentes compositions du mélange initial. Nous avons établi pour chaque composition la courbe du gonflement en fonction du temps. Le temps nécessaire pour atteindre le gonflement limite variait de 40 min. à 2 heures 30 min. pour l'acrylonitrile et le styrène respectivement. Pour ce dernier monomère, nous avions observé dans notre travail antérieur[6] un gonflement plus

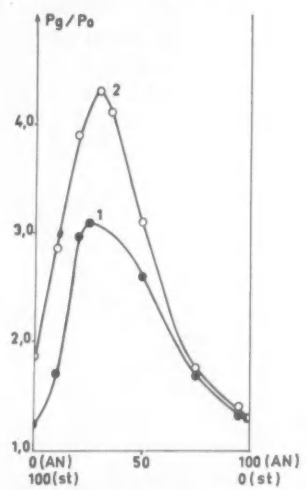

Fig. 1. Variation du taux de gonflement des films de poly(chlorure de vinyle) en fonction de la composition du mélange des deux monomères: (*1*) gonflement après 30 min. de contact; (*2*) gonflement limite.

lent, ce qui indique que le film de Lucoflex utilisé dans le présent travail était différent du film étudié antérieurement.

La Figure 1 montre la variation du taux de gonflement atteint après 30 min. (courbe *1*) ainsi que celle du gonflement limite (courbe *2*), en fonction de la composition du mélange des monomères. On voit que le gonflement des films de poly(chlorure de vinyle) est beaucoup plus important dans les mélanges acrylonitrile–styrène que dans l'un ou l'autre monomère pris séparément.

On peut expliquer ce phénomène en considérant les valeurs des densités d'énergie cohésive δ des trois composants. En effet le δ du styrène (9,2) est plus petit que celui du poly(chlorure de vinyle) (9,5), tandis que le δ de l'acrylonitrile est beaucoup plus grand (11,01). La valeur du δ du mélange des deux monomères au maximum de la courbe de la Figure 1 est égale à 9,7. Cette valeur est voisine du δ du poly(chlorure de vinyle) mais n'est pas égale à ce dernier. Il est vraisemblable que cet écart soit dû aux caractères polaires du polymère et de l'acrylonitrile car la théorie des solubilités basée sur les seules densités d'énergie cohésive n'est applicable en toute rigueur qu'aux composés pour lesquels les effets des polarités sont négligeables.

La vitesse du gonflement est plus petite pour les mélanges riches en styrène que pour les mélanges riches en acrylonitrile. On peut voir en particulier, que pour ces derniers, le taux de gonflement limite est presque atteint après 30 min. de contact (courbes *1* et *2* de la figure).

La Figure 2 montre la variation de la composition du mélange des monomères qui ont pénétré à l'intérieur du film en fonction de la composition du mélange initial utilisé pour le gonflement. On voit que pour des mélanges renfermant plus de 50% d'acrylonitrile, la composition du mélange à l'intérieur du film est pratiquement la même que celle du mélange utilisé pour le gonflement. En revanche, dans le cas des mélanges riches en styrène, le liquide qui pénètre dans le film est fortement enrichi en acrylo-

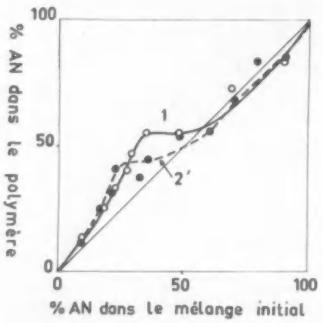

Fig. 2. Variation du taux d'acrylonitrile ayant pénétré dans les films de poly(chlorure de vinyle), en fonction du taux d'acrylonitrile dans le mélange initial: (*1*) après 30 min. de contact; (*2*) à l'équilibre de gonflement.

nitrile. Ce résultat est probablement lié au caractère fortement polaire de ce dernier monomère.

B. Courbes de Conversion du Greffage

Les caractères cinétiques de la réaction de greffage des mélanges d'acrylonitrile et de styrène sont très différents de ceux observés dans le cas du styrène pur.[6] La plupart des courbes de conversion étaient des droites. Les courbes obtenues avec le styrène pur et le mélange renfermant 95% de styrène présentaient une courbure dirigée vers l'axe des abcisses. Nous avions déjà signalé cette particularité dans notre travail antérieur.[6] Dans le cas des mélanges très riches en acrylonitrile, les courbes avaient une forme plus complexe. Dans ces mélanges, le copolymère formé autour des films précipitait au cours de la réaction et ce phénomène compliquait simultanément la cinétique de la copolymérisation et celle du greffage.

En pesant les films immédiatement après l'irradiation, nous avons trouvé que dans la plupart des cas, le gonflement des films en fin de réaction était pratiquement identique au gonflement limite de ces films. Ce résultat montre en particulier que la vitesse de diffusion était grande par rapport à la vitesse de polymérisation, et que par conséquent, la cinétique n'était pas contrôlee par la vitesse de diffusion des monomères. Les détails sur les expériences de gonflement des films greffés seront publiés ultérieurement.

C. Influence de la Composition du Mélange des Monomères

Nous avons irradié des feuillets de poly(chlorure de vinyle) au sein d'une série de mélanges différents styrène–acrylonitrile ainsi que dans les deux monomères purs. La Figure 3 représente la vitesse de greffage en fonction de la composition du mélange des monomères. On voit que lorsque la teneur en acrylonitrile augmente, la vitesse de greffage décroît d'abord brusquement. Elle reste pratiquement constante pour les mélanges contenant 10 à 25% d'acrylonitrile et augmente ensuite. Enfin, la courbe présente une forme complexe pour des teneurs en acrylonitrile supérieures à 85%.

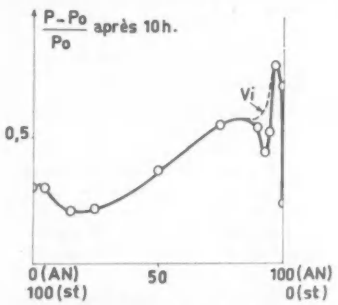

Fig. 3. Variation du taux de greffage après 10 h d'irradiation en fonction de la composition du mélange des monomères. La courbe en pointillés se rapporte aux vitesses initiales de greffage.

D. Copolymérisation

Afin de préciser les raisons de cette complexité de la courbe de greffage, nous avons examiné la cinétique de la copolymérisation radiochimique des deux monomères.

La Figure 4 représente les vitesses de conversion obtenues par dilatométrie en fonction de la composition du mélange des monomères. Les courbes

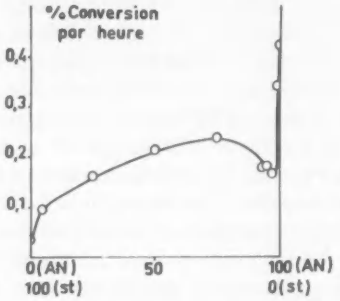

Fig. 4. Copolymérisation radiochimique. Variation de la conversion par heure en fonction de la composition du mélange styrène–acrylonitrile.

de conversion étaient des droites sauf dans le cas des fortes teneurs en acrylonitrile pour lesquelles nous avons trouvé des courbes accélérées. On voit que la vitesse de conversion croît d'abord régulièrement avec la teneur en acrylonitrile dans le mélange, puis elle décroît et présente un minimum aigu pour 97% d'acrylonitrile. Enfin, elle augmente à nouveau, très brusquement, pour les mélanges contenant plus que 97% d'acrylonitrile.

E. Composition des Copolymères Statistiques Styrène–Acrylonitrile et des Branches Greffées

Les résultats, calculés d'après les données de la microanalyse, sont représentés dans le Tableau I.

TABLEAU I

Composition des Copolymères Statistiques et des Branches Greffées sur le Poly(Chlorure de Vinyle) Obtenus pour Différents Mélanges Initiaux de Styrène et d'Acrylonitrile (AN)

AN dans le mélange initial, %	AN dans les branches greffées, %	AN dans le copolymère statistique, %	
		Présent travail	D'après Fordyce et Chapin[8]
25	24	24,1	27
50	28,7	30,0	38
75	32	39,1	47
95	—	57,5	63

Nous avons également porté dans la dernière colonne du tableau les résultats obtenus par Fordyce et Chapin[8] pour la réaction amorcée par le peroxyde de benzoyle à 75°C. On voit que la composition des branches greffées est assez voisine de la composition du copolymère obtenu par voie radiochimique à 20°C (colonne 3). En revanche, les copolymères obtenus par Fordyce et Chaplin[8] renferment systématiquement une teneur plus grande en acrylonitrile. Nous ne connaissons pas pour le moment la raison de ce désaccord.

IV. DISCUSSION

A. Copolymérisation Radiochimique du Styrène avec l'Acrylonitrile

La variation de la vitesse de copolymérisation en fonction de la composition du mélange des monomères suit une loi complexe (Fig. 4). Lorsqu'on ajoute progressivement de l'acrylonitrile au styrène, la vitesse de copolymérisation croît d'abord régulièrement, passe par un maximum, puis décroît. Une courbe de forme analogue a été obtenue par Abkin[9] lors de l'amorçage de la réaction par des initiateurs chimiques à 60° [voir la Figure 7 de la réf. 9]. On peut donc en conclure que ce résultat n'est pas conditionné par le mode d'amorçage utilisé (chimique ou radiochimique). Abkin[9] avait d'ailleur montré que la forme de cette courbe répondait à la relation théorique déduite du schéma cinétique classique en prenant les valeurs suivantes pour les rapports des réactivités des deux monomères:

$$r_1 = K_{AA}/K_{AB} = 0{,}03$$

$$r_2 = K_{BB}/K_{BA} = 0{,}36$$

ou A = AN et B = St.

La forme de cette courbe est donc uniquement déterminée par les vitesses relatives d'addition des monomères sur les chaînes croissantes portant à leur extrêmité active l'un ou l'autre monomère.

Pour les teneurs en acrylonitrile supérieures à 97%, la vitesse de copolymérisation croît brusquement. Abkin[9] n'avait pas observé ce phénomène. Nous pensons que cette accélération est liée à la précipitation du copolymère sous forme de poudre, dans ce domaine de concentrations. Il en résulte en effet une diminution brutale de la vitesse de terminaison, qui conduit à une réaction sans état stationnaire comme celle que l'on observe lors de la polymérisation de l'acrylonitrile pur. Nous avons effectivement obtenu des courbes de conversion accélérées avec ces mélanges. A 60°C, l'acrylonitrile gonfle davantage son polymère et la réaction de terminaison est plus rapide.[10] Cela explique peut-être pourquoi Abkin n'a pas observé d'accélération correspondante.

B. Cinétique du Greffage

En comparant les deux courbes des Figures 3 et 4, on peut noter que l'allure générale du phénomène est la même pour la région médiane des

courbes. En effet, pour des teneurs en acrylonitrile comprises entre 25 et 75%, les vitesses de copolymérisation et de greffage augmentent toutes les deux avec la concentration en acrylonitrile jusqu'à un maximum qui se trouve à 75% d'acrylonitrile pour la copolymérisation et à 80% pour le greffage. Puis les vitesses diminuent, passent par un minimum aigu et croissent brusquement à nouveau.

La courbe de greffage se distingue néanmoins de la courbe de copolymérisation dans deux domaines de concentrations.

a. Pour les mélanges riches en styrène. La vitesse de greffage, au lieu de croître comme celle de la copolymérisation, décroît d'abord et reste pratiquement constante pour des teneurs en acrylonitrile comprises entre 10 et 25%. On peut remarquer que ce domaine de concentrations correspond à un gonflement particulièrement important du film de polymère 10 et 25%. On peut remarquer que ce domaine de concentrations correspond à un gonflement particulièrement important du film de polymère (Fig. 1); on aurait donc pu penser que la vitesse de greffage, qui est donnée à chaque instant par la relation

$$v = k_p [R^\cdot] [M]$$

serait très grande pour ces mélanges car [M] est plus grand. Or l'expérience montre qu'il n'en est rien. Nous pensons que la diminution de vitesse observée dans nos expériences est liée aux perturbations introduites dans le système par l'"effect de gel." En effet, comme la réaction s'effectue dans un milieu très visqueux (le film de polymère partiellement gonflé), il est certain que la terminaison par interaction de deux chaînes croissantes est fortement ralentie. Il en résulte que l'état stationnaire ne s'établit probablement que lentement et que, par conséquent, le nombre des chaînes croissantes présentes à chaque instant augmente au début de la réaction. Dans ces conditions, on devrait observer une réaction autoaccélérée, ce qui ne cadre pas avec la forme linéaire de la plûpart des courbes de conversion. Nous pensons cependant que cette situation, en apparence contradictoire, résulte d'un effet de compensation mettant en jeu deux processus agissant en sens opposé. La caractère autoaccéléré du greffage est compensé par un effet de "freinage", dû peut-être à la nécessité pour le monomère de diffuser dans le film. Nous avions déjà observé des courbes linéaires de ce genre dans d'autres réactions de greffage effectuées dans des conditions analogues et pour lesquelles on pouvait également prévoir un processus autoaccéléré.[11]

Si l'on augmente alors la mobilité des chaînes croissantes, en augmentant, comme nous le faisons ici, le taux de gonflement des films, la réaction de terminaison doit devenir effective et l'effet "retardateur" qui en résulte surcompense l'effet accélérateur dû à l'accroissement de la concentration des monomères. C'est donc à une efficacité accrue de la terminaison que serait due la diminution des vitesses de greffage observée pour les teneurs en acrylonitrile comprises entre 10 et 25%.

Dans le cas du styrène pur et du mélange renfermant 95% de styrène, les phénomènes sont encore plus complexes. Nous avons observé en effet

pour ces deux compositions, des courbes de conversion ayant une courbure dirigée vers l'axe des abcisses, c'est à dire que la réaction est autoretardée (voir aussi Chapiro et al.[6]). L'étude du gonflement des films greffés nous a montré par ailleurs que les films greffés formés dans les mélanges plus riches en acrylonitrile (AN compris entre 10 et 80%) gonflaient d'autant plus dans le mélange réactionnel qu'ils étaient plus fortement greffés, tandis que les films faiblement greffés de styrène et du mélange à 95% de styrène gonflaient moins dans le mélange réactionnel que le film non greffé. Pour des taux de greffage plus élevés, le gonflement de ces derniers films augmentait comme dans le cas des films greffés par un mélange plus riche en acrylonitrile.

Nous pensons qu'on peut expliquer l'ensemble de ces résultats en admettant qu'à 20°C, le styrène, solvant non polaire, ne gonfle le poly(chlorure de vinyle) que dans certaines zones et qu'il ne pénètre pas dans d'autres portions du film, que nous désignerons dans ce qui suit par portions quasi-cristallines. Dans ces conditions, lorsque le monomère se polymérise par greffage, les zones du film accessibles au monomère diminuent, ce qui diminue à la fois le gonflement et la vitesse de greffage. Ensuite, lorsque le taux de greffage augmente, les portions quasi-cristallines sont disloquées par la réaction et deviennent elles-mêmes accessibles au monomère. Le greffage reprend alors avec une vitesse plus grande. (Nous avons effectivement observé un phénomène de ce genre dans un travail précédent.[6]) Si la température de la réaction est plus élevée (60°C), ou si le monomère est plus polaire (acrylonitrile ou méthacrylate de méthyle), le gonflement se fait d'une façon homogène et la réaction ne présente pas de caractére autoretardé.[6,7]

b. Pour les mélanges riches en acrylonitrile. La courbe de greffage (Fig. 3) se distingue également de la courbe de copolymérisation (Fig. 4) en ce que, au lieu de croître rapidement avec la teneur en acrylonitrile, la vitesse de greffage croît d'abord, mais présente ensuite un maximum très aigu pour 97% d'acrylonitrile, puis tombe brusquement. Cette chute de la vitesse se produit dans le domaine de concentrations où le copolymère n'est plus soluble dans le mélange réactionnel et précipite sous forme d'une poudre. Cette poudre gonfle de plus en plus difficilement au fur et à mesure que la composition du mélange s'enrichit en acrylonitrile. L'acrylonitrile pur ne gonfle pratiquement pas son polymère à 20°C et il est vraisemblable que le polyacrylonitrile formé dans le film de poly(chlorure de vinyle) gêne la diffusion ultérieure du monomère.

Nous avons effectivement trouvé que les films greffés d'acrylonitrile gonflaient d'autant moins dans ce monomère que le taux de greffage était plus élevé. La chute de la vitesse de greffage observée pour les mélanges très riches en acrylonitrile est donc probablement due à une diffusion gênée des monomères.

Remarquons que le minimum aigu qui s'observe à 93% d'acrylonitrile (Fig. 3) correspond à une situation très complexe. En effet, les courbes de conversion observées dans ce domaine de concentrations ne sont pas des

droites, mais présentent une forme en *S*. Si l'on considère les vitesses initiales, le minimum de la courbe est beaucoup moins accentué (tracé en pointillés sur la Fig. 3). Ce minimum ne coïncide pas avec le minimum des vitesses de copolymérisation (Fig. 4) mais se produit pour des teneurs plus faibles en acrylonitrile. Ce résultat n'est d'ailleurs pas surprenant, car dans le cas de la copolymérisation, la perturbation est due au passage d'une réaction en phase homogène à une réaction en milieu précipitant, tandis que pour le greffage, la réaction est déjà fortement perturbée par le milieu réactionnel visqueux. Aucune précipitaion apparente ne se produit à l'intérieur des films et la complexité de la cinétique ne résulte probablement que de la modification des nombreux facteurs (mobilité des chaînes croissantes, diffusion des monomères, etc.) qui régissent les réactions en phase gel.

Remarquons enfin que Chandler et collaborateurs,[3] qui ont greffé le même mélange de monomères sur le polyéthylène, ont trouvé une courbe de forme très différente pour les vitesses de greffage, un maximum étant observé pour le mélange 50:50. Il est vraisemblable que dans les conditions expérimentales utilisées par ces auteurs, la cinétique était contrôlee par la vitesse de diffusion des monomères. Cela résulte d'ailleurs de plusieurs remarques exprimées par les auteurs eux-mêmes.

C. Composition des Branches Greffées

Nos résultats dans ce domaine sont encore très fragmentaires. En nous basant sur les données présentées dans le Tableau I, nous pouvons conclure que la composition des branches greffées est très voisine de celle du copolymère formé par polymérisation radiochimique dans un mélange de monomères de même composition. Cette conclusion implique que le milieu gel, dans lequel s'effectue le greffage, n'influe pas sur les rapports des réactivités des deux monomères dans nos conditions opératoires. Notre conclusion est contraire à celle tirée par Odian et collaborateurs[2] des résultats de leurs expériences. Il est vraisemblable que dans les conditions expérimentales utilisées par ces auteurs, la réaction était compliquée par les vitesses de diffusion différentes de chaucun des monomères étudiés. Aucune donnée expérimentale sur les vitesses de diffusion n'est mentionnée dans les publications de ces auteurs.

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Résumé

On a étudié le greffage radiochimique de mélanges de styrène et d'acrylonitrile sur des films de poly(chlorure de vinyle) (PCV) a 20°C. La réaction a lieu dans le gel constitué par le polymère gonflé par les deux monomères. On a trouvé que le taux de gonflement du PCV est notablement plus grand dans certains mélanges que dans l'un ou l'autre monomère pris séparément, le gonflement étant maximum pour le mélange renfermant 30% d'acrylonitrile. La courbe représentant la vitesse de greffage en fonction de la composition du mélange des monomères a une forme complexe. Des études de copolymérisation radiochimique de ces deux monomères ont montré qu'une partie de cette complexité était due à la précipitation du copolymère dans le mélange réactionnel pour des teneurs en acrylonitrile supérieures à 95%. Les differences observées entre les courbes de greffage et de copolymérisation sont interprétées par les perturbations introduites dans la reaction de greffage par l'effet de gel et par la diffusion des monomères. Lorsque les conditions opératoires sont telles que la cinétique du greffage n'est pas contrôlée par la diffusion, la composition des branches greffées est voisine de celle du copolymère statistique obtenu dans le même mélange des deux monomères.

Synopsis

The radiochemical grafting of mixtures of styrene and acrylonitrile into PVC films at 20°C. has been studied. The reaction was carried in the gel of the polymer swollen in the two monomers. It was found that the degree of swelling of PVC is appreciably more pronounced in some mixtures than in one of the pure monomers, the swelling being maximum in a mixture containing 30% acrylonitrile. The curve representing the rate of grafting in function of the composition of the monomer mixture shows a complex shape. The study of the radiochemical copolymerization of these both monomers has shown that this complexity is partly due to the precipitation of the copolymer in the reaction medium for acrylonitrile content higher than 95%. Differences observed between grafting and copolymerization curves were interpreted on the basis of perturbations of the grafting, due to gel effect and to the diffusion of the monomers. When the reaction conditions are such that the grafting kinetics is not diffusion controlled, then the composition of the grafts is similar to that of the statistical copolymer obtained in the mixture of the two monomers.

Zusammenfassung

Die radiochemische Aufpfropfung von Styrol–Acrylnitrilgemischen auf Polyvinylchlorid-(PVC)-filme bei 20°C wurde untersuch. Die Reaktion findet in dem durch Quellung des Polymeren in die beiden Monomeren gebildeten Gel statt. Der Quellungsgrad von PVC in gewissen Mischungen erweist sich als beträchtlich grösser als in jedem der beiden Monomeren; das Quellungsmaximum liegt bei einer Mischung mit 30% Acrylnitril. Es besteht eine komplexe Abhängigkeit der Pfropfungsgeschwindigkeit von der Zusammensetzung der Monomermischungen. Die Untersuchung der radiochemischen Copolymerisation der beiden Monomeren hat gezeigt, dass dieses komplexe Verhalten zum Teil auf die Ausfällung des Copolymeren in der Reaktionsmischung bei Acrylnitrilgehalten höher als 95% zurückzuführen ist. Die zwischen den Pfropfungs- und Copolymerisationskurven beobachteten Unterschiede werden den durch den Geleffekt und die Monomerdiffusion in die Pfropfungsreaktion eingeführten Störungen zugeschrieben. Bei Reaktionsbedingungen, die eine Diffusionskontrolle der Pfropfungskinetik ausschliessen, liegt die Zusammensetzung der aufgep

fropften Zweige in enger Nachbarschaft derjenigen des in der gleichen Monomerenmischung erhaltenen statistischen Copolymeren.

Discussion

N. A. Plate (*Université de Moscow, U.R.S.S.*): Les resultats obtenus par Mme Bonamour sont très interressants car ils donnent la possibilité de comparer la composition de copolymères quand on les greffe, et quand on les copolymèrise en milieu homogène. Les auteurs de cet travail ont montré que la composition du copolymère qui forme les chaînes laterales ne varie pas en comparaison avec la composition du copolymère habituel. Je voudrais ajouter que suivant les resultats obtenus dans notre laboratoire et aussi par Odian aux Etats-Unis s'il existe une adsorption séléctive d' un des deux monomères sur une surface quelconque (polymère ou non), la composition des chaînes polymériques est différente de celle que l'on obtient par copolymérisation radicalaire simple. Cela est dû à la difference de la microconcentration des deux monomères à l'endroit exact de l'amorçage. Cet effet ne peut-être observé sans doute que pour les conversions très petites car après la situation tend à devenir plus ou moins homogène. Les resultats obtenus dans le travail de Mme Bonamour peuvent peut-être l'expliquer par cette observation.

A.-M. Jendrychowska-Bonamour: Odian et coll. n'ont pas verifié que dans leurs conditions expérimentales la réaction n'était pas influencée par les vitesses de diffusion des deux monomères et cette circonstance peut peut-être expliquer les differences de composition observées par ces auteurs.

A. Chapiro: Dans notre travail nous avons trouvé une légère différénce entre la composition des branches greffées et celle du copolymère statistique formé dans des conditions analogues (Tableau I) mais nous n'avons pas attaché d'importance à ce resultat. Cependant nous avons trouvé plus recemment que si l'on effectue le greffage à 50°, la composition des branches greffées diffère notablement de la composition du copolymère statistique.

J. Dobó (*Institut de Recherches des Matières Plastiques, Budapest, Hungary*): I think that in systems rich in styrene, the grafting under conditions of limited swelling of the substrate by styrene can cause the graft copolymer or the polystyrene side chains even to get below their glass transition points. This supposition would help to explain not only the limited amount of grafting, but the strong effect of temperature too.

A. Chapiro et A.-M. Jendrychowska-Bonamour: Cette interprétation de M. Dobó rejoint l'explication proposée dans le texte de notre communication, mais il est necéssaire de comprendre pourquoi le poly (chlorure de vinyle) greffé de styrène à 20°, gonfle moins dans ce monomère que le polymère non greffé et pourquoi cette particularité ne se retrouve plus pour le copolymère greffé à 50°.

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Grafting on Polypropylenes of Different Microstructures

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INTRODUCTION

The investigation of Chapiro and others[1–5] suggested to us that the method of preirradiation with γ-rays in the presence of air can be applied effectively to graft different monomers onto polypropylene fibers.[6,7]

The purpose of our investigations was first of all to get a polypropylene fiber with improved dyeability and water absorption. These requirements could be achieved in so far that with different monomers and varying degrees of grafting the dyeabilities, water absorptions and melting points could be altered over a wide range. The mechanical properties changed only slightly during the grafting procedures.

In our previous papers[6–8] we have investigated the mechanism of the γ-ray-induced grafting on polypropylene fibers as a function of the irradiation intensity, the applied dose, the kind and concentration of the monomers, and other grafting conditions. During these investigations we could find definite connections between these functions.

Investigation of the cross sections of various grafted and dyed polypropylene films, monofilaments, and fibers by means of a microphotometer indicated that the grafting begins on the surface and it penetrates only later into the substance. The limit of this grafting is when we get a substance which is equally grafted through its whole cross section.[8] The rate of the penetration of the grafting into the sample is determined by the rate of diffusion of the monomer and the shape of the sample. With the same irradiation dose the thinner samples (0.1 mm. thick film) are grafted through more quickly than the thicker ones, for example, monofilament which is 2 mm. in diameter.

During these investigations we made the interesting observation that the rate of grafting is quite different in oriented and unoriented polypropylene fibers. Grafting on unoriented fibers can be achieved readily in comparison to the oriented fibers made from the same samples despite the fact that the latter have a smaller diameter.

EXPERIMENTAL

Polypropylene Fibers and Films

Polypropylene fibers and films were produced from polypropylene granules (Moplen AS-50, Montecatini) and from some samples prepared on a laboratory scale. The fibers were produced by extrusion after the extraction of the various light and heat stabilizers which might interfere with our measurements, principally by hindering the formation of peroxide bonds. The extrusion of the monofilaments and fibers was carried out at temperatures of 240–260°C. at different rates of winding to produce fibers having various degrees of crystallinity. The extrusion device had three heating zones and a ratio of the diameter to the length of the screw of 1:22. Multifilaments were produced with an 8 hole die.

When orienting the samples, the monofilaments and fibers were stretched in boiling water to ratios of 1:5 and 1:8 by means of a drawing device which had two series of three cylinders which moved with different velocities.

Measurement of Crystallinity

The percentage of crystallinity was calculated on the basis of density measurements. The density was estimated in a density-gradient tube which consisted of a mixture of carbon-tetrachloride and toluene. The crystallinity was calculated from eq. (1):

$$\text{Crystallinity } \% = 100[(V_a - V)/(V_a - V_c)] \quad (1)$$

where V_a is the specific volume of the amorphous polypropylene fiber = 1.1765 ml./g.), V_c is the specific volume of the totally crystalline polypropylene fiber (= 1.0684 ml./g.), and V is the specific volume of the sample.

The values of V_a and V_c were determined with the help of x-ray investigations.[9]

Irradiation

The irradiations were carried out with a 345-C Co^{60} source at room temperatures, with an intensity of about 15,000 r/h. The time of irradiation varied from 20 to 150 hr. However, the sample used for infrared investigations was irradiated with an intensity of 241,000 r/hr.

Grafting

The grafting on the previously irradiated samples was carried out with the usual method[6–8] in an oxygen-free atmosphere in the presence of methyl-methacrylate monomer at 80°C. for 1 hr.

Determination of Peroxide Content

The content of peroxide groups in the sample was determined iodometrically with the solvents given by Beati, Severini, Toffano[10] (toluene,

chloroform, HI, and 0.01*N* sodium thiosulfate) but in the glass apparatus described by Sully.[11] The peroxide contents given in Table I are averages of six measurements.

Infrared Measurements

The infrared spectroscopical investigations were carried out with a Zeiss IR-10 type spectrometer (Carl Zeiss, Jena).

Electron Spin Resonance Measurements

The ESR measurements were kindly made by the Central Chemical Research Institute of Hungarian Academy of Sciences on an instrument built at that laboratory.

RESULTS AND DISCUSSION

We have already mentioned that the investigations were carried out in order to improve the water absorption and dyeability of polypropylene fibers. In searching for a technology we have investigated at what step of the fiber formation (before extrusion, after extrusion, after drawing, etc.) the irradiation and the grafting take place. During these investigations in which the penetration rate into the irradiated polypropylene sample was also studied, we found the anomalous behavior of the unstretched and stretched samples.

In order to estimate which parameters other than diffusion of monomer influence the dependence of the grafting on the crystallinity, we have measured the peroxide contents of monofilaments and fibers with different degrees of crystallinity which were irradiated in the presence of air. The peroxide group contents were determined iodometrically. The rate of oxidation was followed by means of infrared spectroscopy and the rate of generation of free radicals as a result of irradiation was measured by ESR spectroscopy.

On irradiation of polypropylene in the presence of air, initially free radicals are generated, which later on react with the oxygen to form hydroperoxides and/or diperoxide groups.

All these reactions must be controlled by the inner structure of the polymer which on the one hand governs the diffusion of oxygen to the free radicals and on the other hand enables the hydrogen generated by the irradiation to diffuse out. Hence according to our conception the microstructure of the polymer has an influence on: (*1*) recombination of free radicals by their reaction with hydrogen, through altering of the diffusion of hydrogen from the sample, which naturally increases with increasing intermolecular distance between single molecules in the sample; (*2*) lifetime of the free radicals, which in a dense (crystalline) microstructure could either take part in a recombination reaction or because of the difficulty of diffusion remain as a "stable" free radical until it comes in contact with a reactive medium; (*3*) formation hydroperoxide or diperoxide

groups which are then controlled by the diffusion of oxygen to the free radicals. The peroxides and hydroperoxides formed during the irradiation could be destroyed by the irradiation itself or as a result of their low stability, forming more stable oxygen-containing groups on the macromolecule such as keto or aldehyde groups. We have attempted to get more information on the conditions within the polypropylene fiber during the irradiation, the effect of the microstructure on these reactions. The goal of all these investigations was determination of the optimal conditions of grafting during commercial fiber production.

The values given for the oxygen contents in Table I show that these are dependent on the shape of the sample. The powdered polypropylene (sample 1) and the thin monofilament (samples 2, 2-1, 2-2) contains much more oxygen than the monofilament which received a greater irradiation

TABLE I
Variation of the Oxygen Content and Grafting as a Function of Microstructure and Irradiation Conditions

Sample no.	Sample type	Draw ratio	Diameter of polypropylene fibers, mm.	Crystallinity, %	Irradiation dose, Mr	O_2 content, %	Yield of grafting %[a]
1	Powder				0.3	0.195	
I	Unstretched monofilament		0.98	50.0	0.3	0.038	13.3
I-1	Stretched monofilament	1:5	0.48	58.0	0.3	0.050	3.7
IV	Unstretched monofilament		0.74	52.5	1.5	0.192	95.7
V-1	Stretched monofilament	1.5	0.71	61.0	1.5	0.123	11.0
2	Unstretched fiber		0.060	54.5	1.5	0.342	136.8
2-1	Stretched fiber	1:5	0.028	68.5	1.5	0.429	83.0
2-2	Stretched fiber	1:8	0.021	72.5	1.5	0.440	43.4
II	Unstretched monofilament		0.80	53.5	2.3	0.341	117.0
II-1	Stretched monofilament	1:5	0.36	62.5	2.3	0.427	87.6
II-2	Stretched monofilament	1:8	0.25	55.5	2.3	0.571	145.0
III	Unstretched monofilament		0.65	51.5	2.3	0.401	142.2
III-1	Stretched monofilament	1:5	0.28	60.5	2.3	0.595	117.3
III-2	Stretched monofilament	1:8	0.19	54.0	2.3	0.875	186.0

[a] Calculated as $100 (W - W_0)/W_0$, where W_0 is the original weight of the sample and W is the weight of the sample after grafting.

dose, but has a larger diameter (samples III, III-1, III-2). The oxygen content on the other hand is also dependent on the crystallinity of the sample. Samples with nearly the same diameter but different crystallinities (samples IV and V-1) show some difference in their oxygen contents. Those with a lower crystallinity have a higher oxygen content than those which have a higher crystallinity, although the difference is not very large. The grafting is more pronounced in the last cases (samples IV and V-1 or II-2 and III-1).

These data indicate that the increase in the number of peroxide groups (oxygen percentage) is controlled by the diffusion of the oxygen into the samples, but from this point of view the crystallinity has a smaller influence than the thickness of the sample, as the crystalline dimensions permit a nearly free motion of oxygen atoms. The O_2 molecule can move more easily among the crystalline regions than the much larger monomer molecule. Above all these the oxygen diffusion could not be correctly investigated and there was surely a certain amount of oxygen dissolved in the polymer before the irradiation since extrusion and fiber formation and a well as irradiation were carried out in the presence of air.

The results in Table I show that grafting depends on the amount of the peroxide groups (the greater the irradiation dose, the greater the peroxide content, the greater the rate of grafting) (samples I-1, V-1, II-2), but it is also dependent on the crystallinity and diameter, that is, on the relative surface of the sample. The crystalline structure offers a great hindrance to the diffusion of the monomer molecule, and this fact determines the grafting. This explains why the unoriented samples can be grafted to a higher extent than the fibers made from the same samples by stretching them to a certain extent. Although this operation increases their specific surface a more crystalline (dense) structure is concomitantly formed which hinders the monomer diffusion.

In this connection it is very interesting to show another fact: from the literature[16] on polypropylene fiber production it is known that for certain crystalline configurations an increase of the stretching ratio over a certain limit, decreases the crystallinity. This could also be observed by us, as the samples produced with a stretching ratio of 1:5 possess higher crystallinity than those which were produced with a disco ratio of 1:8. It is supposed that in this case the crystals once formed, are broken up by the stress; this supposition is proved by the means of grafting. In our opinion three factors influence in this case the higher grafting ratio: (*a*) The increase of the relative surface; (*b*) the increase of the amorphous region through breaking up of crystals (possibility of forming microcrystals); and (*c*) the production of free radicals by mechanical means since breaking of crystals may mean breaking of chemical bonds.

Infrared Investigation

We tried to follow the formation of hydroperoxide and/or C=O groups by means of infrared spectroscopy. First studied were 20 μ films which

had a crystallinity of 70%; subsequently multifilaments were also investigated. The measurements proved that in the region of radiation dose usually applied by us (0.3–2.5 Mr), the infrared spectroscopy cannot prove the presence of C=O or OH groups. With doses of about 40 Mr, we could get spectra where C=O groups could be observed with certainty and the OH group begins to appear (Fig. 1). According to the literature,[12,13] the

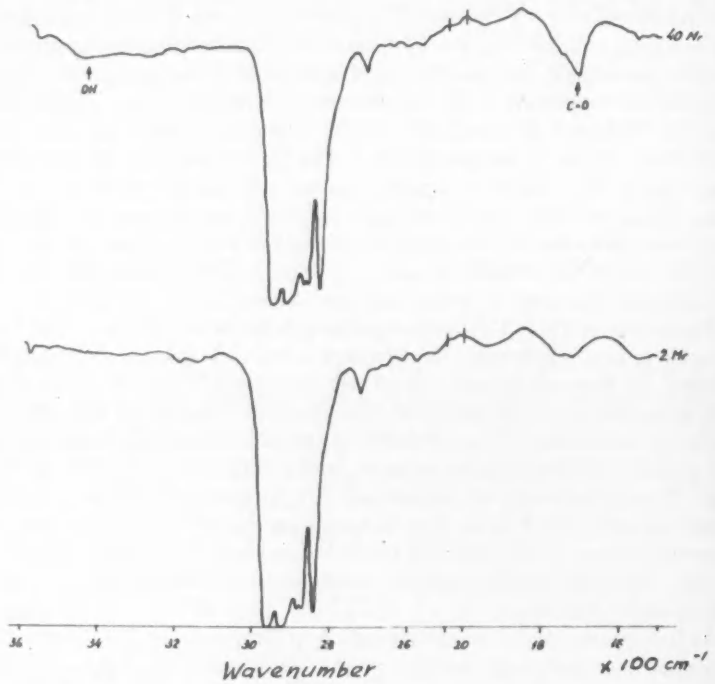

Fig. 1. Infrared spectrum of polypropylene films irradiated in the presence of air.

absorption of the C=O group should appear at 1710 cm.$^{-1}$, and the absorption of the OH group, supposed to be the OH group of the hydroperoxide, should appear at 3550–3420 cm.$^{-1}$.

The films and fibers which were irradiated with 40 Mr became quite brittle and were not useful for our purposes. As this method could not be used to show the quantitative differences of the percentage of oxygen contents in the undrawn and drawn polypropylene fibers, we did not try to use this method further for our investigations.

ESR Investigations

In polypropylene samples which are irradiated in the presence of air, not all of the free radicals react with oxygen; thus some of them can be

identified with ESR spectroscopy. We measured the free radicals in samples which were irradiated in the presence of air, at room temperature with an irradiation dose of 0.5 Mr shortly after the irradiation with a spectrometer operating at 473 KHz.

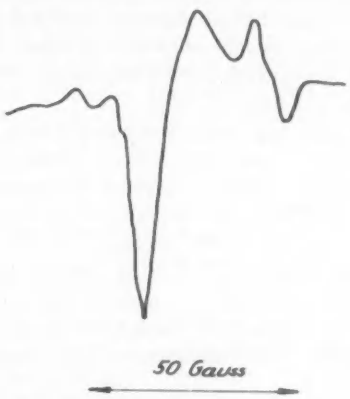

Fig. 2. ESR spectrum of undrawn polypropylene monofilaments. Irradiation and measurement at room temperature.

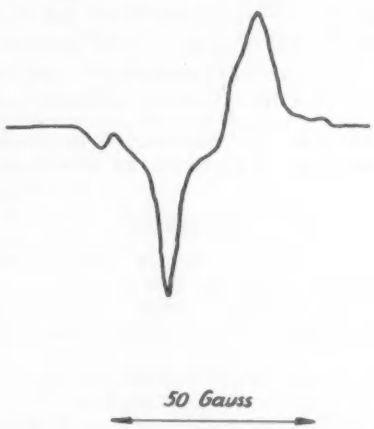

Fig. 3. ESR spectrum of drawn polypropylene monofilaments. Irradiation and measurement at room temperature.

The measurement showed certain differences in the spectra of the free radicals in the unstretched specimen and in a sample stretched to a disco ratio of 1:5. For the undrawn specimen (Fig. 2) we found the asymmetric spectrum which is characteristic for the free radicals formed from peroxide groups; the drawn samples showed a symmetrical spectrum (Fig. 3).

These results are in good agreement with those of Fischer and Hellwege,[14] who found that the differences are more pronounced in the unstretched and stretched samples if the studies are carried out *in vacuo*, and so their measurements may give conclusions on the structure of the free radicals formed at extremely low temperatures. These authors also found that, for oriented isotactic polypropylene samples irradiated at low temperatures or room temperature, rotating the sample through an angle of 90° caused a change in the spectra, i.e., they found a dependence between the direction of stress and the axis of the magnetic field.

They did not find quantitative differences between the number of free radicals in the stretched and unstretched samples. Ballantine[4] and Kashiwabara[15] investigated polyethylenes with different degrees of crystallinity and showed that at room temperature the free radicals are mostly located in the crystalline part of the polymer. This explains according to them the greater free radical contents of the more highly crystalline polyethylene samples. The variation in crystallinity was not produced by orientation through stretching but they have investigated low and high pressure polyethylenes. The quantitative differences in the two samples are not mentioned.

Our further work on this problem we intend to limit to ESR measurements. Unfortunately at present the measurements cannot be carried out in the region which would be best for our purposes. The irradiations and measurements at low temperatures which can be carried out safely cannot be transposed without criticism to what happens at room temperatures. So the picture is somewhat complicated and much work must be done to select precisely the different factors influencing the grafting.

We wish to thank Mr. Radics and Mr. Holly of the Central Chemical Research Laboratories for their kind help with the ESR and infrared spectroscopical measurements.

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Synopsis

In our previous investigations we have studied the γ-ray induced grafting of several monomers onto polypropylene monofilaments and fibers. We found that the unoriented polypropylene fibers, monofilaments, and films which were prepared without stretching can be grafted to a greater extent with fibers and films with an oriented microstructure. We measured the change in grafting ability as a function of the crystallinity of the samples. Fibers and films with different crystallinities and orientations were achieved by alternating the method of preparation and the degree of stretching (orientation). By alternating the diameter of monofilaments, varying the temperature of the production of the samples, and working with different draw ratios we could obtain materials in which the degree of crystallinity, size of crystals, and degree of orientation was different. The samples were irradiated with γ-rays from a Co^{60} source with the same intensity to total dose. For grafting materials we used acrylic acid and methyl methacrylate. Also in studying the grafting reaction we measured the peroxide and hydroperoxide contents of the irradiated samples by means of iodometric analysis and infrared spectroscopy. The quantity of free radicals induced by the radiation was followed by the electron spin resonance method. With the two methods we could follow the rate of the appearance and disappearance of free radicals in the irradiated matter and the rate of formation and the stability of peroxide and hydroperoxide groups. We also investigated the rate of the penetration of the grafted frontier into polypropylene fibers of different degrees of crystallinity; this is a function of the rate monomer diffusion velocity and the concentration of free radicals or peroxide (hydroperoxide) groups inside the samples. All of these circumstances were investigated as function of the mechanical properties, dyeability, and water absorption of grafted polypropylene fibers.

Résumé

Au cours de nos précédentes recherches, nous avons étudié la réaction de greffage enduite par les rayons-gamma de plusieurs monomères sur des monofilaments et fibres de polypropylène. Nous avons établi que les fibres non-orientées de polypropylène de même que les monofilaments et lames minces préparés sans étirement peuvent subir un greffage plus important que les fibres et lames à microstructure orientée. Nous avons mesuré la variation de l'aptitude au greffage en fonction de la cristallinité des échantillons. Les fibres et lamelles possédant différentes cristallinités et orientations ont été obtenues par variation de la méthode de préparation et du degré d'étirement/orientation. En alternant le diamètre des monofilaments et en faisant varier la température de préparation des échantillons, de même qu'en faisant varier les rapports d'étirement, nous avons pu obtenir des matériaux dont le degré de cristallinité, la dimension des cristaux et l'orientation étaient différentes. Les échantillons ont été irradiés avec une source de Co^{60} avec la même intensité la même durée. Comme substance à greffer nous avons utilisé de l'acide acrylique et du méthacrylate de méthyle. En vue d'expliquer la réaction de greffage, nous avons simultanément mesuré la teneur en peroxyde et hydroperoxyde des échantillons irradiés au moyen d'une analyse iodométrique et par spectroscopie infra-rouge. La quantité de radicaux libres induits par le rayonnement a été suivie par la méthode de résonance électronique magnétique. Au moyen de ces deux méthodes, nous avons pu suivre la vitesse d'apparition et de disparition des radicaux libres dans la substance irradiée et la vitesse de formation de groupes peroxydiques et hydroperoxydiques et leur stabilité. Nous avons aussi étudié la vitesse de pénétration du front de greffage à l'intérieur des fibres de polypropylène de cristallinité différente, elle est fonction de la vitesse de diffusion du monomère et de la concentration en radicaux libres, ou de groupes peroxyde/hydroperoxyde dans les

échantillons. Tous ces aspects ont été étudiés en fonction des propriétés mécaniques de moyens de teinture et de la possibilité d'absorber de l'eau des fibres de polypropylène greffé.

Zusammenfassung

In früheren Arbeiten wurde die γ-Strahl-induzierte Aufpfropfung mehrerer Monomerer auf Polypropylen-Monofils und Fasern untersucht. Es wurde gefunden, dass nichtorientierte Polypropylenfasern und-monofils ebenso wie ohne Reckung hergestellte Folien einer Aufpfropfung in grösserem Ausmass zugänglich sind als Fasern und Folien mit orientierter Mikrostruktur. Die Abhängigkeit der Aufpfropfungfähigkeit von der Kristallinität der Proben wurde gemessen. Fasern und Folien mit verschiedener Kristallinität un Orientierung wurden durch Variierung der Herstellungsmethode und des Streckungsgrades (Orientierung) erhalten. Durch Änderung des Monofildurchmessers und der Herstellungstemperatur der Proben sowie durch Anwendung verschiedener Reckungsverhältnisse konnten Stoffe mit verschiedenem Kristallinitätsgrad, Kristallgrösse und Orientierungsgrad dargestellt werden. Die Proben wurden mit einer Co-60-Quelle mit der gleichen Intensität im gleichen Ausmass bestrahlt. Zur Aufpfropfung wurden Acrylsäure und Methylmethacrylat herangezogen. Gleichzeitig mit der Pfropfungsreaktion wurde der Peroxyd- und Hydroperoxydgehalt der bestrahlten Proben jodometrisch und infrarotspektroskopisch bestimmt. Die Menge der durch die Strahlung induzierten freien Radikale wurde mit Hilfe der Elektronspinresonanzmethod gemessen Mit diesen beiden Methoden konnte die Bildungs- und Abklinggeschwindigkeit der freien Radikale in der bestrahlten Substanz sowie die Bildungsgeschwindigkeit von Peroxyd- und Hydroperoxydgruppen und deren Stabilität bestimmt werden. Weiters wurde die Eindringgeschwindigkeit der Pfropfungsgrenze in Polymerfasern mit verschiedener Kristallinität untersucht, welche eine Funktion der Diffusionsgeschwindigkeit des Monomeren und der Konzentration freier Radikale oder Peroxyd-(Hydroperoxyd)-gruppen im Inneren der Probe ist. Der Zusammenhang der erwähnten Grössen mit den mechanischen Eigenschaften, der Anfärbbarkeit und der Wasserabsorption von aufgepfropften Polypropylenfasern wurde untersucht.

Discussion

C. S. Hsia Chen (*American Cyanamid Co., Stamford, Conn.*): In our work in grafting of chloromethylstyrene to polypropylene fiber (Stamm, Hostermann, Felton, and Chen, *J. Appl. Polymer Sci.*, **7**, 753 (1963)) when we compare the degree of swelling of the fiber and the decrease in birefringence of the swollen fiber we have concluded that the swelling occurs only in the amorphous region of the fiber. Therefore, the grafting occurs only in the amorphous regions also. Do you have similar data to support this?

F. Geleji: We also found this effect. When enlarging the crystalline amount the grafting is lower. By investigating the crystal structure of the grafted polymer we found it unchanged, which shows that the grafting takes place only in the amorphous phase.

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Radiation-Induced Graft Copolymerization onto Cellulose and Polyvinyl Alcohol Fibers with Binary Mixtures of Comonomers

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Introduction

In previous papers we have reported grafting of styrene, methyl methacrylate, and butadiene onto cellulose and polyvinyl alcohol (PVA) fibers.[1–4] The presence of a small amount of water in the system or the addition of methanol to monomer generally accelerates the grafting reaction. The micro- and ultramicrostructures of the cellulose gel strongly affects the ease and extent of the reaction in a complicated manner, and we can not simply conclude that more amorphous cellulose reacts more readily than the less amorphous forms.

We wish now to report the extension of these studies to the cases of the graft copolymerization of butadiene–styrene, butadiene–acrylonitrile, styrene–acrylonitrile, and other binary monomer mixtures onto cellulose and PVA fibers.

EXPERIMENTAL

Materials

Regular and high tenacity viscose staple fibers were obtained from Toho Rayon Co., while polynosics and Egyptian cotton were supplied from Toyo Spinning Co. All these cellulosic fibers were purified by extraction with hot benzene–ethanol (1:1). The properties of the fibers are given in Table I. PVA and high density polyethylene fibers were prepared in our laboratory by a conventional method; the denier of the fibers was 1.51 and 300, respectively.

A commercial grade of butadiene and reagent grades of methanol, styrene, and acrylonitrile were used after redistillation.

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TABLE I
Properties of the Cellulosic Fibers

Fiber	Denier	Tenacity, g./den.		Elongation, %		Degree of crystallinity, %[a]
		Dry	Wet	Dry	Wet	
A. Regular viscose rayon	1.51	2.60	1.81	16.4	20.3	44
B. High tenacity rayon	1.51	3.75	2.97	23.1	30.7	44
C. Polynosics	1.55	3.83	2.74	13.8	14.9	55
D. Egyptian cotton	1.50	4.10	3.42	9.2	10.5	58

[a] Determined by an x-ray method.

Methods

Fibers (50 mg.) were in most cases immersed in methanol solutions (5 ml.) containing comonomer and irradiated *in vacuo* in the 1000-curie Co^{60} source of the Osaka Laboratories of the Japanese Association for Radiation Research on Polymers at a dose rate of 8.5×10^3 r/hr. to the desired dosage. Preirradiation was performed with electrons from a 1.5 m.e.v. Van de Graaff accelerator in air. The dose rate was 4×10^4 rad/sec. and the total dose 3.6 Mrad. The irradiation was carried out discontinuously to avoid heating of the sample. After the preirradiation the samples were subjected to grafting, which was carried out using the same mixture as in the case of the mutual grafting.

The fibers were removed from the solution after various periods of contact with the comonomer, thoroughly washed with benzene or dimethylformamide, and dried to a constant weight. The amount of grafted copolymer was taken to be equal to measured increase in weight.

For the determination of the composition of the grafted and nongrafted copolymers, only those comonomer mixtures were used that contained acrylonitrile as a component, and the reaction was conducted only to an extent of 4% conversion. The acrylonitrile content of the copolymers was calculated either from nitrogen content or from optical density at 4.4μ by infrared analysis of the copolymers.

RESULTS AND DISCUSSION

1. Graft Copolymerization of Butadiene–Styrene

Mixtures of styrene and butadiene were graft polymerized onto cellulose fibers. The experimental technique involved mutual γ-irradiation of polymers immersed in methanol solutions of the comonomer. The grafted samples were freed of homocopolymer by solvent extraction and the per cent graft was calculated. The details of these procedures are given in the experimental section. Except at the very initial stages of the grafting process, the reaction does not proceed as surface grafting, but as volumetric

one, i.e., chain propagation occurs in the viscous polymer–monomer medium.[1,5]

Figure 1 shows experimental results of grafting onto regular viscose rayon. In the experiments, the total concentration of comonomers was kept constant while the composition of comonomers was varied. The reaction was carried out at 30°C. in vacuum. It may be seen from Figure 1 that on addition of a small amount of butadiene to styrene the per cent graft was enormously increased, although butadiene itself undergoes

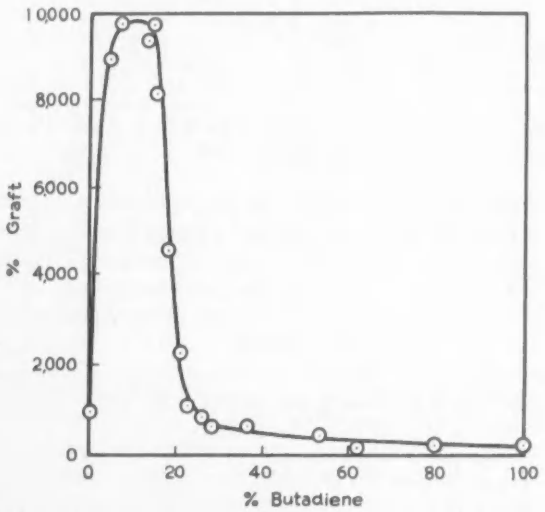

Fig. 1. Grafting of styrene–butadiene onto regular viscose rayon. Concentration of comonomer = ca. 50%; dose rate = 8.5×10^3 r/hr.; total dose = 1.4 Mr; irradiation temperature = 30°C.

grafting to a very small extent. Values of the total conversion and graft efficiency are given in Table II, together with the per cent graft for the same experiments as in Figure 1. It is noteworthy that the graft efficiency is very high, in certain cases the per cent graft reaches several thousands. The highest per cent graft was ca. 10,000; this means that the graft polymer consists of one part of the backbone and one hundred parts of the grafted copolymer.

Radiation-induced homocopolymerization of butadiene–styrene was carried out under the same conditions as shown in Table II in the absence of cellulose; the results are shown in Figure 2. In this case the conversion decreases monotonically with increasing addition of butadiene to styrene. It may be concluded that the maximum of the curve in Figure 1 may be attributed to the fact that the reaction takes place in gel. In order to know whether the composition of the comonomer or that of the grafting mixture containing methanol is more important for the appear-

TABLE II
Grafting of Styrene–Butadiene onto Regular Viscose Rayon[a]

Monomers in comonomer mixture, wt.-%		Comonomer concn., %	Graft, %	Total conversion, %	Graft efficiency, %
Butadiene	Styrene				
0	100	46.6	957	97.4	7.1
5.8	94.2	53.3	9,780	97.8	78.4
12.7	87.3	54.0	9,290	89.8	81.6
18.0	82.0	54.1	4,500	49.8	73.3
22.1	77.9	52.3	1,540	24.6	59.0
25.9	74.1	53.6	890	17.3	53.1
52.8	47.2	59.1	446	8.5	55.3
100	0	56.4	72.5	—	—

[a] Conditions: concentration of comonomer = ca. 50%; dose rate = 8.5×10^3 r/hr.; total dose = 1.4 Mr.; irradiation temperature = 30°C.

ance of the maximum, experiments were carried out for the various concentrations and compositions of comonomer; results are summarized in Figure 3. It may be seen from Figure 3 that the composition of comonomer plays the most important role in the graft copolymerization. The optimum composition lies in the range of 3–22% butadiene contents and is independent of the comonomer concentration.

We then examined the influence of microstructure of cellulose fibers on grafting. The following four kinds of cellulose were employed for the

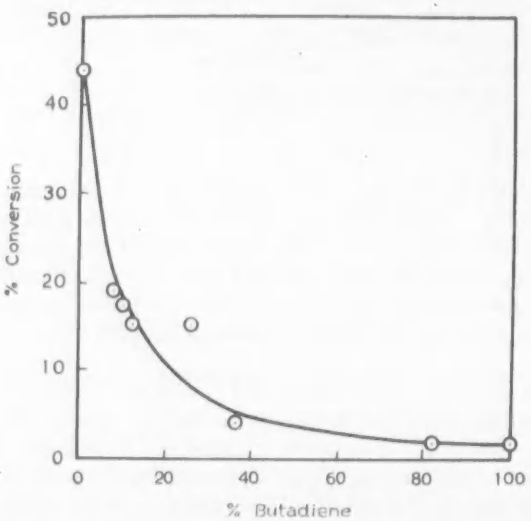

Fig. 2. Radiation-induced homocopolymerization of styrene–butadiene. Concentration of comonomer = ca. 50%; dose rate = 8.5×10^3 r/hr.; total dose = 1.34 Mr; irradiation temperature = 30°C.

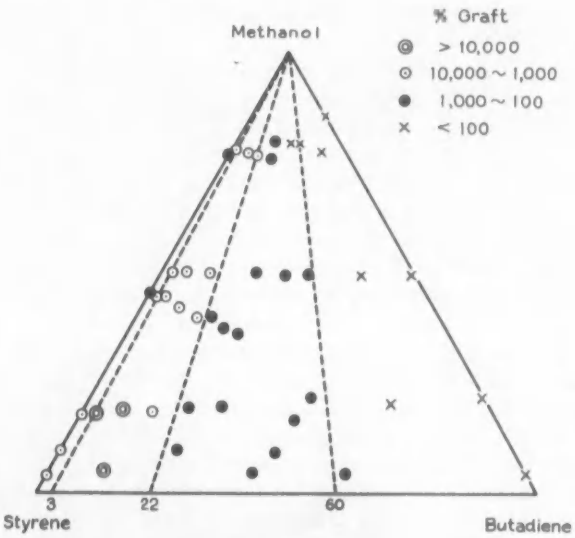

Fig. 3. Grafting of styrene–butadiene onto regular viscose rayon using methanol as a solvent.

experiments: regular viscose rayon (A); high tenacity viscose rayon (B); polynosics (C); cotton (D). Part of the experiments is shown in Table III. It may be seen that different microstructures lead to differences in case of grafting, while there is no doubt that the maximum per cent grafting of all kinds of cellulose lies in the range 5–25% butadiene content.

TABLE III
Grafting of Styrene–Butadiene onto Various Cellulose Fibers (A = Regular Viscose Rayon; B = High Tenacity Viscose Rayon; C = Polynosics; D = Cotton)[a]

Butadiene in comonomer mixture, wt.-%	Graft, %			
	A	B	C	D
0	957	102	—[b]	282
5	9,300	250	—[b]	470
10	9,010	420	760	340
15	9,700	—	2,100	230
20	3,200	500	1,250	125
25	830	1,920	370	—
30	650	880	220	61
50	490	190	75	43
75	73	105	26	23
100	41.3	45.2	22.8	17.4

[a] Conditions: concentration of comonomer = ca. 50%; dose rate = 8.5×10^3 r/hr.; total dose = 1.4 Mr; irradiation temperature = 30°C.

[b] Fibers were disintegrated.

Polynosics lose their fiber structure at a smaller butadiene content and disintegrate.

For a comparison with the grafting by the mutual irradiation technique, experiments were also carried out by preirradiation. Regular viscose rayon was irradiated in air with electron beams from a Van de Graaff generator to a dose of 3.6 Mrad and subjected to grafting in vacuum at 50°C. for 168 hr. in the same grafting mixture as given in Table II. Generally the degree of grafting was very low and decreased monotonously from pure styrene to pure butadiene and no maximum was observed. It is noteworthy that a large amount of so-called "popcorn" polymer was formed as nongraft copolymer at the composition where the maximum was observed by grafting by the mutual irradiation technique. In the case of catalytic grafting with peroxides, the results were similar, and popcorn polymer was formed.

The remarkably high grafting is, undoubtedly, closely connected with popcorn polymerization. As to the mechanism of the popcorn formation,[6-8] the following explanation is generally accepted. The first step in the unseeded reaction is probably the formation of a tiny insoluble cross-linked nucleus, which acts as a network in which other chains become entangled, or from which chains start growing, initiated either by radicals or activated double bonds in this gel structure. Perhaps backbone cellulose fibers take the place of the tiny insoluble network, and chains start growing from radicals formed by irradiation in the gel structure of cellu-

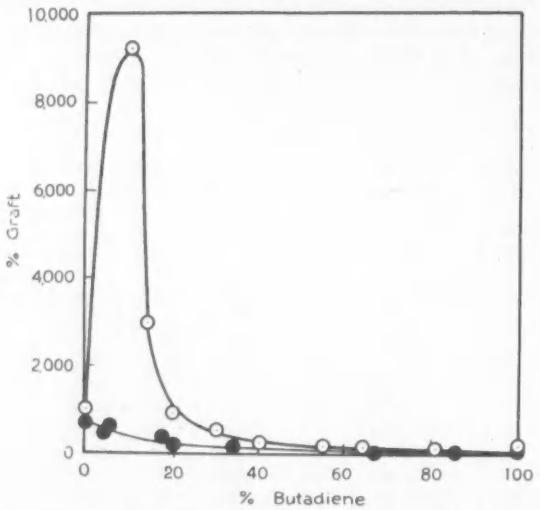

Fig. 4. Grafting of styrene–butadiene onto PVA and Polyethylene Fiber. (○) PVA, comonomer concentration = 50%, dose rate = 8.5×10^3 r/hr., total dose = 1.2 Mr, irradiation temperature = 40°C.; (●) polyethylene, comonomer concentration = 50%, dose rate = 8.5×10^3 r/hr., total dose = 1.5 Mr, irradiation temperature = 30°C.

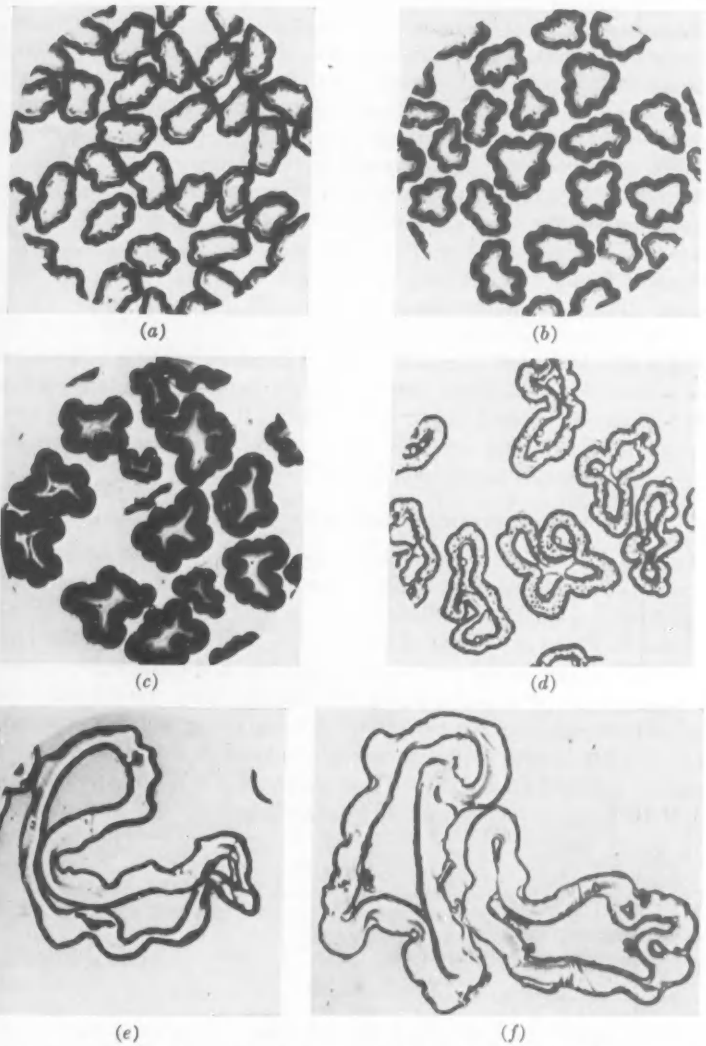

Fig. 5. Cross sections of regular viscose rayon after grafting with butadiene–styrene at various per cent grafting: (*a*) O (original fiber); (*b*) 67.8%; (*c*) 235%; (*d*) 557%; (*e*) 4417%; (*f*) 9081%. The cross sections were dyed with Azine Brilliant Blue 6B.

lose. According to this simple explanation we are led to the conclusion that all grafting reactions with mutual irradiation are a kind of popcorn polymerization. However, this is not true. Only when swelling of the gel, formation of radicals in the gel, and homocopolymerization are in delicate balance may a popcorn polymerization like grafting be observed.

Using the same binary comonomer mixtures as for cellulose fibers, experiments were carried out for grafting onto PVA and polyethylene fibers. As is shown in Figure 4, PVA behaves quite similarly to cellulose, whereas in the case of the grafting onto polyethylene not only was the degree of grafting low but also no maximum was observed on the per cent graft versus comonomer composition curve.

Butadiene–methyl methacrylate and butadiene–methyl acrylate showed essentially the same behavior as butadiene–styrene, but no detailed experiments were carried out.

Figure 5 shows cross sections of the original and grafted regular viscose rayons. The per cent grafting ranges from 128 (Fig. 5*b*) to 9081 (Fig. 5*f*). All sections were dyed with Azine Brilliant Blue 6B, a dyestuff which colors only the skin of rayon. Up to the highest degree of grafting, the skin and core structures of the fibers may be clearly differentiated, although the skin can not be colored above 235% graft. The cross-sectional area is enlarged but the form is kept unchanged; there is nothing of the irregular shape which reminds us of a popcorn polymerization.

2. Graft Copolymerization of Butadiene–Acrylonitrile

The binary mixture of butadiene–acrylonitrile seems to be interesting because both components of the comonomer have only a small tendency to be grafted onto cellulose or PVA.

Table IV shows experimental results of the grafting onto regular viscose rayon with a fixed concentration of comonomer and changing composition of comonomer. Without addition of butadiene, acrylonitrile was rapidly grafted onto cellulose, but the extent of the grafting was very low and increased quite slowly with increasing amount of the irradiation. For example, per cent graft was 11.8% at a dose of 5.0×10^4 r and 16.1% at 2.1×10^5 r. At a higher dose only nongraft polymer was formed, and the

TABLE IV
Grafting of Acrylonitrile–Butadiene onto Regular Viscose Rayon[a]

Butadiene in comonomer mixture, wt.-%	Comonomer concn., %	Total dose, $r \times 10^{-5}$	Graft, %
0	50.4	2.1	16.1
0	50.4	9.9	Gel
10.9	50.7	2.1	103
19.5	53.2	9.9	Gel
30.2	46.4	"	2,710
43.6	51.8	"	10,600
63.6	43.2	"	13,020
73.2	51.6	"	2,350
88.3	50.4	"	197
100	56.4	"	72.5

[a] Conditions: concentration of comonomer = ca. 50%; dose rate = 8.5×10^3 r/hr.; irradiation temperature = 30°C.

whole mass of the grafting mixture was turned into a continuous, insoluble gel through crosslinking. Up to a comonomer composition of about 20% butadiene, the general feature of the reaction was similar to the grafting with pure acrylonitrile. It was impossible in these cases to separate the graft polymer for the determination of per cent graft. The reaction proceeded smoothly above 20% butadiene contents, and a maximum was observed near 50%. The per cent graft was about 10,000% at the maximum. The mechanism of copolymerization of butadiene–acrylonitrile seems to be essentially the same as that of butadiene–styrene.

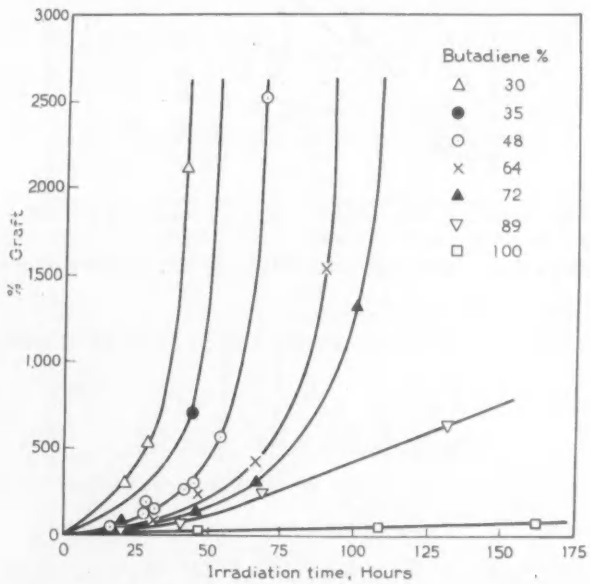

Fig. 6. Effect of comonomer (butadiene–acrylonitrile) composition on the grafting rate. Concentration of comonomer = ca. 80%; dose rate = 8.5×10^3 r/hr.; irradiation temperature = 30°C.

The rate of grafting was measured at a comonomer concentration of 80% because it had been found that the grafting occurred with higher rates at higher comonomer concentrations. The experimental results are shown in Figure 6. Six curves in the figure correspond to six different comonomer compositions. Curves corresponding to comonomer compositions at which very high degrees of grafting are observed reflect apparently the autocatalytic character of the reaction. This leads to the following differential equation:

$$dx/dt = k_1 a + k_2 x \tag{1}$$

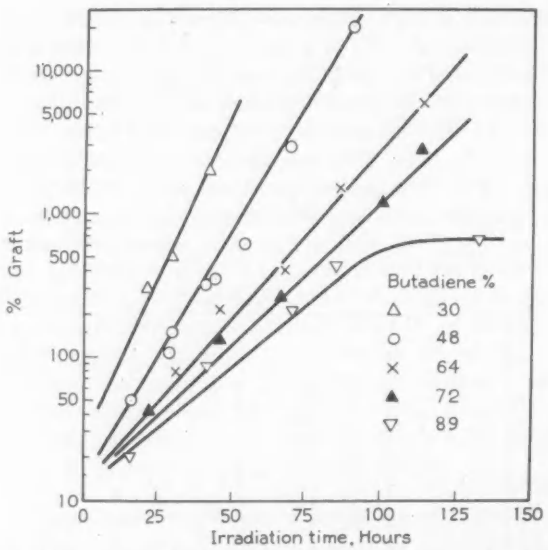

Fig. 7. Semilogarithmic representation of the relation between per cent graft and grafting time.

where a is the mass of backbone polymer and x is the mass of graft at time t.

Integration of eq. (1) yields:

$$k_2 t = \log (k_1 a + k_2 x) - \log k_1 a \tag{2}$$

Except for the very beginning of the reaction, eq. (2) may be simplified to

$$k_2 t = \log k_2 x - \log k_1 a \tag{3}$$

This equation was also derived by Dobó et al.[9] for the grafting, and is essentially the same as that employed for popcorn polymerization. $(x/a) \times 100$ corresponds to per cent graft. Figure 7 gives log (per cent graft) versus time curves. As expected, linear relationships are found for the grafting with comonomer compositions at which a very high degree of grafting occurs.

The influence of temperature on the rate of grafting was studied and the results are shown in Figure 8. The rate constant for grafting k_2 was calculated from eq. (3). The apparent activation energy for the grafting was found to be 3.0 kcal./mole.

The influence of dose rate on the rate of grafting was also studied, and the results are shown in Figure 9. The data given in Figure 9 leads to the relationship;

$$\text{grafting rate} = K\ (\text{dose rate})^{0.6} \tag{4}$$

The value of 0.6 seems to be quite reasonable.

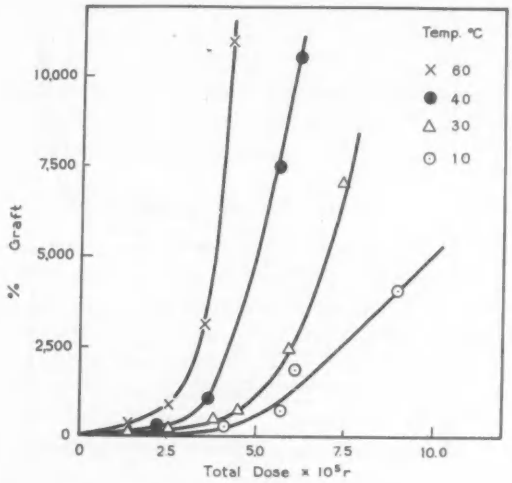

Fig. 8. Effect of irradiation temperature on the grafting of butadiene–acrylonitrile onto regular viscose rayon. Dose rate = 8.5×10^3 r/hr.; butadiene: acrylonitrile methanol = 40:40:20.

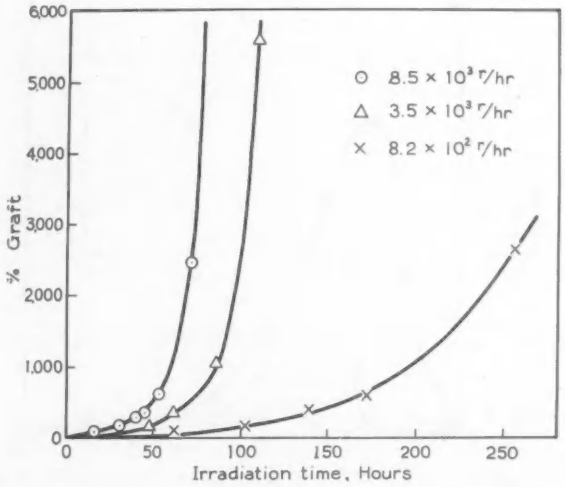

Fig. 9. Effect of the dose rate on the grafting of butadiene–acrylonitrile onto regular viscose rayon. Butadiene:acrylonitrile:methanol = 40:40:20.

The compositions of the grafted and nongrafted copolymers were determined by infrared analysis, and results are shown in Figure 10. The composition of the nongrafted copolymer which is formed during the grafting lies near to the values calculated employing the reactivity ratios

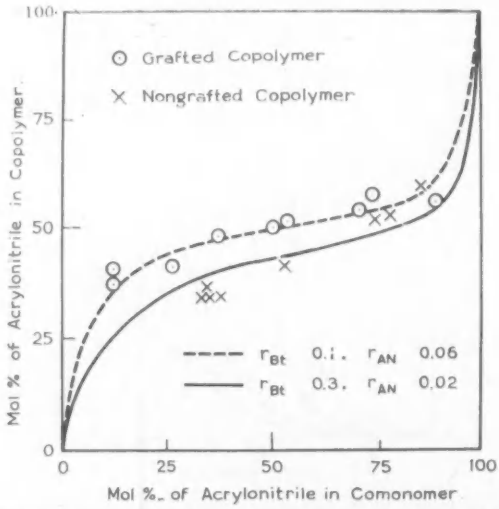

Fig. 10. Relation between composition of comonomer mixture (butadiene–acrylonitrile) and composition of grafted and nongrafted copolymer.

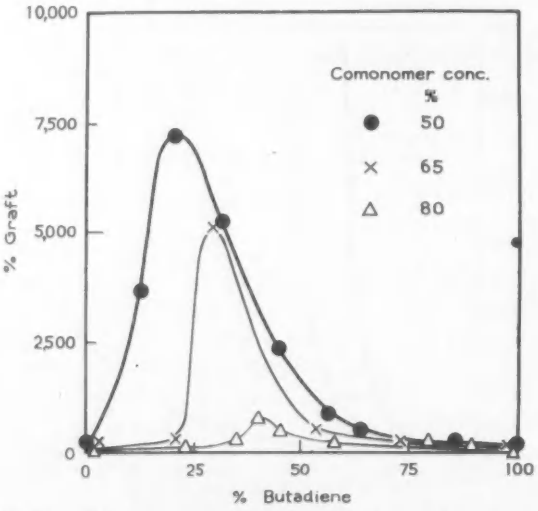

Fig. 11. Grafting of butadiene–acrylonitrile onto PVA fiber. Dose rate = 8.5×10^3 r/hr.; total dose = 5.7×10^5 r; irradiation temperature = 40°C.

r_1 (butadiene) = 0.3 and r_2 (acrylonitrile) = 0.02, whereas the grafted copolymers are richer in acrylonitrile. In this case, the reactivity ratios, $r_1 = 0.1$, and $r_2 = 0.06$, fit better to the experimental results. This finding is in good agreement with that obtained by Odian et al.[10,11] for radiation-

induced grafting of binary mixtures onto polyethylene and Teflon films. It seems probable that the polymer gel absorbs preferentially more polar monomer.

The behavior of PVA fibers for the grafting with this binary mixture was similar to that of cellulose. Figure 11 shows the dependence of per cent graft on the monomer composition for PVA.

3. Graft Copolymerization of Styrene–Acrylonitrile

The binary mixtures which were employed for the grafting in the foregoing experiments contain as one component butadiene, which is known to play an important role in popcorn polymerization. We studied therefore grafting with styrene–acrylonitrile, a binary mixture which does not contain diene compound as a component. Figure 12 shows part of such experiments. In this case also a maximum of per cent graft was observed at a composition of 50–75% acrylonitrile. The per cent graft was much lower than 10,000%, and the highest value was about 2,500%.

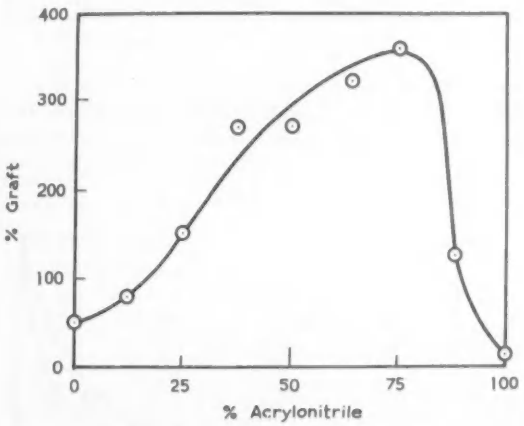

Fig. 12. Grafting of styrene–acrylonitrile onto regular viscose rayon. Concentration of comonomer = 50%; dose rate = 8.5×10^3 r/hr.; total dose = 1.1×10^5 r.

Figure 13 shows the grafting rate. The curves do not display typically autocatalytic features and seem to flatten out at higher doses. The graft efficiency was also generally low and lies between 15 and 20%.

Analysis of grafted and nongrafted copolymers was also carried out for this system, and the results are shown in Figure 14. Monomer reactivity ratios are apparently different for grafted and nongrafted copolymer, and the grafted copolymers were richer in acrylonitrile. Similar results were also obtained for PVA.

It is not always necessary that two components of binary liquid mixture are monomers, to exhibit an extraordinarily favorable condition for grafting

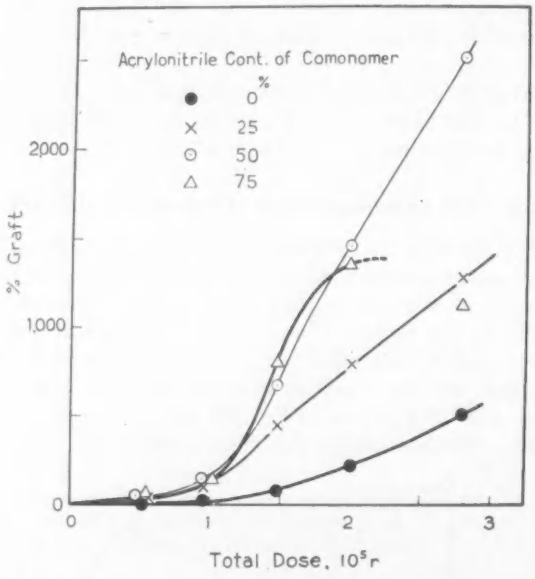

Fig. 13. Effect of comonomer (styrene–acrylonitrile) composition on the grafting rate. Concentration of comonomer = 50%; Dose rate = 8.5×10^3 r/hr; irradiation temperature = 30°C.

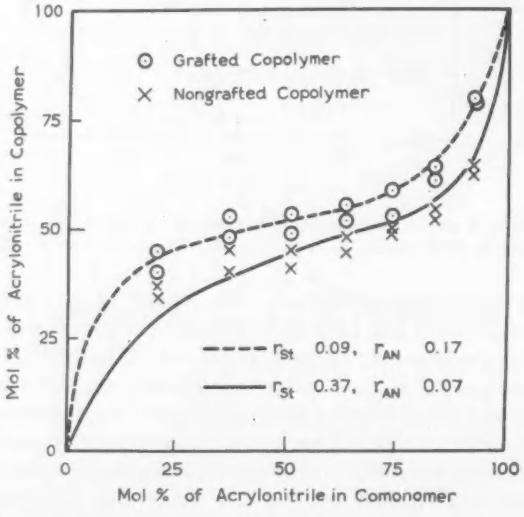

Fig. 14. Relation between composition of comonomer mixture (styrene–acrylonitrile) and composition of grafted and nongrafted copolymer.

at a certain composition. As was shown in previous papers,[3,12] binary mixture of styrene–methanol shows a marked maximum at a certain composition. It is probable that this phenomenon is not especially interesting, for, as was shown and discussed by Chapiro,[13] this binary mixture shows maxima and a minimum even for radiation-induced homopolymerization; however, we think that the maximum for graft polymerization has no direct connection with the maxima for homopolymerization because even a binary mixture which does not show a maximum for homocopolymerization can exhibit a very marked maximum for graft copolymerization.

4. Graft Copolymerization of Butadiene–Styrene–Acrylonitrile

Graft copolymerization of a ternary mixture, butadiene–styrene–acrylonitrile, onto cellulose was also studied, and it was found that the grafting proceeds at a very high rate at comonomer concentrations in the range of 50–80% and a comonomer composition of butadiene:styrene:acrylonitrile = 1:3:3. Some 20,000% graft was possible in favorable cases without losing fiber structure of cellulose. The experiments are summarized in Table V.

TABLE V
Grafting of Butadiene–Styrene–Acrylonitrile onto Regular Viscose Rayon[a]

Total dose, $r \times 10^{-5}$	Composition of comonomer mixture			Graft, %
	Butadiene, %	Styrene, %	Acrylonitrile, %	
2.0	63	26	11	62
"	45	15	40	116
"	16	13	71	251
"	12	40	48	356
4.1	76	13	11	105
"	47	28	25	750
"	37	14	49	1,265
"	22	14	63	3,634
"	13	52	35	4,828
"	7	44	49	6,863
"	10	54	36	9,215
5.9	18	44	38	23,360
7.3	19	43	38	27,630
9.4	24	40	36	21,550

[a] Conditions: concentrations of comonomer = ca. 80%; dose rate = 8.5×10^3 r/hr.; radiation temperature = 30°C.

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Synopsis

Experiments on radiation-induced graft copolymerization of binary mixtures such as butadiene–styrene, butadiene–acrylonitrile, styrene–acrylonitrile and some other systems onto cellulose and PVA fibers were carried out with the use of methanol as a solvent. A very marked maximum of per cent graft was observed in every case at a certain composition of the comonomer mixture. It seems that such a marked maximum is closely connected with popcorn polymerization for the case of butadiene–styrene, but popcorn polymerization is not a necessary condition for the appearance of the maximum. Only a delicate, combined effect of swelling of the gel, formation of radicals in the gel, homocopolymerization, and some other unknown factors might lead to a very high degree of grafting.

Résumé

On a effectué des expériences de copolymérisation greffée, induite par radiation, de mélanges binaires tels de butadiène–styrène, butadiène–acrylonitrile, styrène–acrylonitrile et quelques autres systèmes sur des fibres de cellulose et de PVA en présence de méthanol comme solvant. Un maximum très net du pourcentage de greffé a été observé dans chaque cas pour une certaine composition du mélange de comonomères. Il semble qu'un tel maximum prononcé soit intimement lié avec une polymérisation locale dans le cas du butadiène–styrène; cela n'est toutefois pas une condition nécessaire à l'apparition du maximum. Seule la combinaison de divers effets tels le gonflement du gel, la formation de radicaux dans le gel, la homocopolymérisation et d'autres facteurs inconnus peuvent amener à un degré de greffage très élevé.

Zusammenfassung

Versuche über die strahlungs-induzierte Pfropfcopolymerisation von binären Mischungen, wie Butedien–Styrol, Butadien–Acrylinitril, Styrol–Acrylnitril und einigen anderen Systemen, auf Cellulose- und PVA-Fasern wurden mit Methanol als Lösungsmittel ausgefügrt, In jedem Falle wurde bei einer bestimmten Zusammensetzung der Monomerenmischung ein sehr ausgeprägtes Maximum der Pfropfungsausbeute beobachtet. Beim System Butadien–Styrol ist dieses ausgeprägte Maximum eng mit der Popcornbildung verknüpft, jedoch ist die Popcornbildung nicht eine notwendige Voraussetzung für das Auftreten des Maximums. Nur ein fein abgestimmter, kombinierter Einfluss der Quellung des Gels, der Bildung von Radikalen im Gel, der Homocopolymerisation und einiger anderer unbekannter Faktoren kann zu einer hochgradigen Aufpfropfung führen.

Discussion

M. Terra (*France*): (*1*) Quelles sont les qualités mécaniques des filmes cellusosiques après greffage?

(*2*) Quelles sont les qualités mécaniques des fibres de PVA avant et après greffage?

(*3*) Les fibres de PVA utilisé étaient-elles acétalisées ou non. Si non, quelle est leur solubilité dans l'eau après greffage?

I. Sakurada: As to the mechanical properties of grafted PVA fibers, they are more resilient and elastic when the per cent grafting is not too high (50–100%). At higher per cent grafting, the tenacity becomes low.

The original PVA fiber is soluble in hot water. When the per cent grafting is not too high, the grafted fiber is partly soluble in boiling water.

The PVA fibers were not acetalyzed nor did they contain residual acetyl groups.

S. H. Pinner (*B.X. Plastics, Essex, Great Britain*): I wish to invite comments from Prof. Sakurada and Dr. Chapiro concerning the significance of the difference in reactivity ratios of a pair of monomers when irradiated in solution or in the solid state while adsorbed in a polymer substrate, as first demonstrated by Odian. There are two possibilities: (*1*) Diffusion control of accessibility of growing free radical to one or the other monomer. (*2*) Alteration of nature or reactivity of active centres due to influence of polymer substrate.

If the reaction truly proceeds by free radical propagation and the discrepancies are only due to diffusion control, what are the implications with respect to the composition of the grafts? There are various possibilities.

(*1*) The grafted chains have the statistical distribution predictable from the reactivity ratios.

(*2*) The grafted chains have a non-random distribution, if they correspond more closely to block copolymers.

(*3*) Initially random copolymer grafting occurs, but subsequently the new copolymer chains graft on to the copolymer side chains rather than to the parent polymer.

Finally, can one accurately determine reactivity ratios from experiments in the solid state? One normally determines reactivity only after very low conversions, whereas in solid state polymerization, a large proportion of the adsorbed monomer mixture is converted. Has the integrated form of the copolymer equation been used to calculate r_1 and r_2?

It appears that much more work needs to be done on copolymerization in the solid state in view of its bearing on primary radiation reactions.

A. Chapiro (*C.N.R.S., Bellevue, S. & O., France*): Je suis tout à fait d'accord avec M. Pinner que les problèmes de copolymérisation en phase gel ou en milieu semi-solide sont loin d'être résolus et ce sont d'ailleurs de telles considérations qui ont motivé nos expériences dans ce domaine. Nous avons trouvé maintenant que les rapports de réactivité de deux co-monomères peuvent être modifiés sans que l'on puisse mettre en cause les phénomènes de diffusion. Nous ne connaissons pas pour le moment la raison des différences observées.

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Graft Polymerization on Cellulosic Materials. Part I. Cation-Exchange Membranes from Paper and Acrylic Acid

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1. INTRODUCTION

Several methods have been described in the literature for the polymerization of vinyl monomers in cellulosic materials. Such methods all involve the generation of a free radical on the cellulose molecule, and four general types of procedure are available. The radical may be generated by either ultraviolet,[1] α- or β-irradiation.[2] A cellulose derivative with a high transfer efficiency may be utilized to produce suitable radicals.[3] The radical may be generated by the decomposition of a suitably unstable cellulose derivative (e.g., azo[4]), and fourthly the cellulose molecule may be oxidized by suitable reagents to initiate polymerization, preferably by hydrogen abstraction from the cellulose. The latter method is particularly attractive from a practical point of view, provided degradation of the cellulose can be kept to a sufficiently low level, and various oxidants have been used, such as molecular oxygen,[5] ozone,[6] ceric ion,[7–13] hydroxyl radical (from hydrogen peroxide and ferrous ion),[14] and periodate ion.[15] In addition, boron trifluoride has been used to initiate graft polymerization on cellulose.[16]

Despite the multiplicity of methods which have been described for such polymerization of vinyl monomers in cellulosic materials, there is virtually no unambiguous proof that the added vinyl polymer is truly grafted, i.e., attached by covalent bonding, to the cellulose. The products of such reactions, however, are normally resistant to extraction by solvents which would be expected to dissolve the vinyl homopolymer and for many practical purposes this is the requirement which determines the utility of the product. It is our intention therefore in this series of papers to attempt to clarify some aspects of the mechanism of polymerization in cellulosic materials, particularly by chemical methods such as those outlined above, to investigate the properties of the products, and in some cases to seek proof of covalent grafting.

One possible novel use for vinol grafted cellulosics is the preparation of ion-exchange membranes based on paper, and the present paper is concerned with the achievement of this end by the grafting of acrylic acid on paper. Paper-based ion-exchange membranes have been prepared pre-

viously[17] by impregnation of kraft paper with formaldehyde condensation polymers, and in this type of treatment there is probably some reaction between cellulose and methylol groups, so that these membranes may also be regarded as containing graft copolymers.

A practical ion exchange membrane must have wet strength, permselectivity, and adequate electrical conductivity. Paper, however, has a high nonselective permeability towards ions in aqueous solution, and this is reduced in the present method by the simultaneous blocking of interfiber pores and introduction of ion-exchange groups by graft polymerization.

2. EXPERIMENTAL

Materials

Parchmentized paper, used throughout this work except where indicated, was obtained from the Vegetable Parchment Mills (Delcroix) Ltd. and was made from a bleached mixed hard and soft wood sulfate pulp parchmentized for 1–2 sec. in 60–70% sulfuric acid and had a weight of 67 g./m.^{2} In some experiments Whatman No. 1 chromatographic paper (98–99% α-cellulose) and an unglazed high wet-strength urea-formaldehyde kraft paper were used. Monomers were distilled before use, and the ceric ammonium nitrate was of Analar quality.

Graft Polymerizations on Paper

Polymerizations were carried out in degassed aqueous solution in vacuum. A 5 cm. square (0.1600 g.) of paper in 20 ml. standard acid containing the required amount of monomer (usually 1 ml.) with 1 ml. 0.1M ceric ammonium nitrate (this concentration of oxidant, $5 \times 10^{-3}M$, was used throughout) in a separate container were frozen and thawed several times in vacuum to remove dissolved oxygen. After mixing, the solutions were shaken in a thermostat at 25 ± 0.1°C. for the required polymerization time. The papers were removed, washed with 5N sulfuric acid to remove sorbed ceric ions, then with water and methanol and dried at 40°C./5 mm. over $CaCl_2$. The graft polymers were extracted with an appropriate solvent for the homopolymer, viz., boiling benzene for polymethyl acrylate, water at 80°C. for polyacrylic acid, and N,N-dimethylformamide at 80°C. for polyacrylonitrile.

Hydrolysis and Crosslinking

Grafted papers containing polymethyl acrylate were hydrolyzed with 2.5N sodium hydroxide solution at 15 ± 2°C. for 18 hr. to convert the ester into polysodium acrylate. This was converted into the acidic form by washing with 5N sulfuric acid, washed with water and methanol, and dried at 40°C./5 mm. over $CaCl_2$.

Dried papers containing polyacrylic acid were crosslinked by refluxing 5 min. with a solution (0.3 moles/l.) of toluene 2,4-diisocyanate (2×10^{-3} moles/g. paper) in sodium-dried benzene.

Membrane Characterization

Ion-exchange capacities were determined by the method described by Helfferich[18] using 50 mg. samples of grafted paper. Measurements of the free-diffusion flux were determined in a cell similar to that described earlier,[19] between water and 1.5% (w./v.) sodium chloride solution at 25°C. Membrane resistance was measured[19] in flowing 0.6*N* potassium chloride solution at 25°C. with the use of platinized platinum electrodes and a Wayne-Kerr B221 Universal bridge operating at 1592 cycles/sec.

3. RESULTS AND DISCUSSION

One of the most convenient methods of graft polymerization on cellulose is that of Mino and Kaizerman[7] involving use of ceric ion initiation in aqueous acid, and this is the method which has been used throughout the present work. The choice of paper is governed by the requirement that a paper with some wet strength is essential for any kind of aqueous chemical processing, we have therefore only considered three types of paper in our work, viz. parchmentized paper, filter paper, and paper containing wet strength additive. The last is not likely to be suitable for any fundamental approach to the problem, since the chemistry of the system is considerably complicated by the additives such as urea-formaldehyde resins and rosin, and in any case graft polymerization does not occur readily on urea-formaldehyde bonded wet strength kraft paper (see Fig. 1.). Filter paper can be grafted very rapidly (Fig. 1) but its porous nature would inevitably

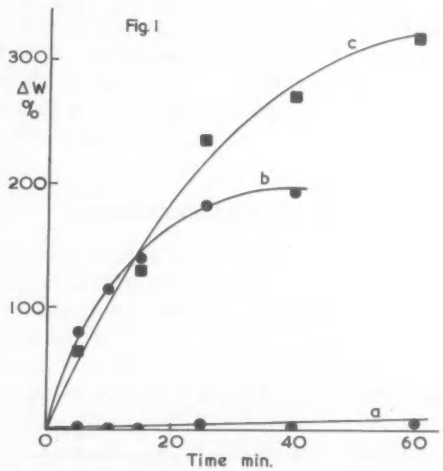

Fig. 1. Graft polymerization of methyl acrylate on various papers: (*a*) kraft paper with urea–formaldehyde resin additive; (*b*) parchmentized paper; (*c*) Whatman No. 1 filter paper. [MA] = 0.55 *M*; [HNO_3] = 0.1 *M*. All papers extracted with boiling benzene for 2 hr. after grafting.

present problems in limiting free diffusion in the derived membrane. We have therefore carried out most of our work on a bleached acid-parchmentized paper which has the advantages of high wet strength and relatively low permeability, although its reactivity at higher graft levels towards the ceric initiated grafting system is rather less than that of filter paper (Fig. 1). This effect is almost certainly due to its lower water uptake and consequent smaller area of contact with the reaction solution.

The added polymer was almost entirely resistant to extraction with solvent (Table I), and this fact, although not unequivocal proof, is a strong in-

TABLE I
Solvent Extraction of Grafted Papers[a]

Monomer	ΔW, %	Extraction solvent[b]	Change in wt. during extraction, %
Methyl acrylate	78	Benzene	−1
Methyl acrylate	193	Benzene	−0.5
Methyl acrylate[c]	123	Benzene	−4
Methyl acrylate[c]	340	Benzene	−5
Acrylonitrile	17	Dimethylformamide	+1
Acrylonitrile	38	Dimethylformamide	+1
Acrylic acid	4	Water	0
Acrylic acid	7	Water	0

[a] Grafting conditions: [monomer] = 0.55 M; [HNO_3] = 0.1N.
[b] Extraction at 80°C., 2 hr.
[c] Using Whatman No. 1 paper.

dication that the bulk of the added polymer is covalently attached to the paper. This is further substantiated in the experiments described below, by the retention of polyacrylic acid in paper which has been grafted with methyl acrylate and subsequently saponified in 10% sodium hydroxide, a solvent which is known to be capable of extracting hemicelluloses from paper fibers.

Effect of Acid Concentration

The effect of acid concentration on rate of grafting has been studied in the system paper–ceric ammonium nitrate–acrylonitrile–sulfuric acid, and is shown in Figure 2. The maximum in grafting rate at ca. 0.25N acid does not appear to have been reported previously, although it has been observed[13] that the rate decreases above pH ca. 1.0. It has also been noted[11] that in the oxidation of butane-2,3-diol with ceric salts, the rate increases with acid concentration up to ca. 0.25N, but in this system no decrease in rate occurs at higher acid normalities.

There is insufficient evidence to speculate in detail on the causes of the maximum in Figure 2, but it seems probable that the initial increase in rate with acid concentration is due to decreasing concentration of ceric–hydroxyl ion complexes, which by analogy with ferric salts,[20] would be ex-

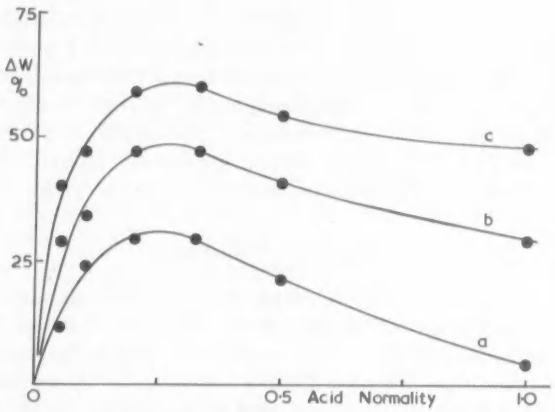

Fig. 2. Graft polymerization of acrylonitrile on parchmentized paper. Effect of sulfuric acid concentration at [AN] = 0.75 *M* and various grafting times: (*a*) 10 min.; (*b*) 25 min.; (*c*) 60 min.

pected to be more effective than ceric ion itself in radical termination. The decrease in rate with further increasing acid concentration may be due to a decreased concentration of the solid-state cellulose–ceric complex, which is generally assumed[11,13] to be formed as an intermediate.

Rate of Grafting with Various Monomers

The graft polymerization of three different monomers on paper has been studied in detail, viz., acrylic acid, acrylonitrile, and methyl acrylate (Fig. 3). The rate of grafting increases markedly in the order shown, as does the total amount of polymer which can be added to the paper.

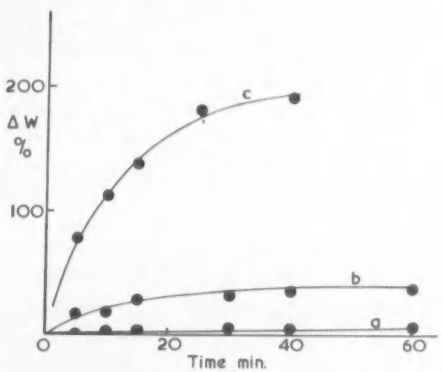

Fig. 3. Graft polymerization of various monomers on parchmentized paper. (*a*) acrylic acid; (*b*) acrylonitrile; (*c*) methyl acrylate. [monomer] = 0.55 *M*; [HNO_3] = 0.1*N*.

With acrylic acid it is assumed that the low rate and limitation in total add-on is due to the progressively increasing sorption of both Ce^{4+} and Ce^{3+} by the graft copolymer, and a similar effect is also possible to a smaller extent with acrylonitrile, by complexing of Ce^{4+} and Ce^{3+} with the nitrile groups. This type of effect, which may be postulated as operating either by reduction of ceric ion in solution or by influencing the termination reactions, would be expected to be minimized with methyl acrylate.

Membrane Properties

The predominant difficulty in preparation of the membranes described herein is the reduction of diffusion of the coion through the membrane, i.e., reduction of free diffusion. With methyl acrylate as the grafting monomer it was found that the grafted paper was virtually impermeable to sodium and chloride ions ($D = < 1 \times 10^{-7}$ meq./cm.^{2} sec. at $\Delta W = 125\%$). However on alkaline hydrolysis to liberate the acrylic acid group the membrane became highly swollen and permeable ($D = 3.0 \times 10^{-4}$ meq./cm.^{2} sec.) and it was evident that the saponification had reopened the interfiber pores in the paper. An attempt was therefore made to reduce the swelling, by crosslinking the acrylic acid paper in nonaqueous solution with toluene-2,4-diisocyanate. The resultant membrane then had a free diffusion value of $D = 8.3 \times 10^{-6}$ meq./cm.^{2} sec., and resistance 4.0 ohm/cm.^{2}. Such membranes appear to have suitable electrical and mechanical properties for general use.

In view of the above observation that grafting with a hydrophobic mono-

TABLE II
Membranes from Graft Polymerization of Acrylonitrile–Acrylic Acid Mixtures on Paper[a]

	AN:AA monomer molar ratio = 2:1				AN:AA monomer molar ratio = 1:1			
	5 min.	15 min.	30 min.	120 min.	5 min.	15 min.	30 min.	120 min.
ΔW, %	18.2	27.1	31.5	45.3	10.9	18.6	28.9	43.7
N, %	2.46	3.50	4.20	5.14	1.07	1.93	2.76	4.07
Capacity, meq./g.	0.66	0.83	0.99	1.19	0.55	1.03	1.25	1.61
Acrylonitrile content, %	9.3	13.2	15.9	19.5	4.0	7.3	10.5	15.4
Acrylic acid content, %	4.7	6.0	7.1	8.6	4.0	7.4	9.0	11.6
Ratio AN/AA in graft (w/w)	1.98	2.20	2.24	2.27	1.01	0.99	1.17	1.33
Water uptake, %	80	76	61	50	85	83	70	62
Free diffusion $\times 10^6$, meq./cm.^{2} sec.	9.1	4.3	0.95	0.95	18.2	15.7	9.1	0.8
Resistance, ohm/cm.^{2}	5.8	9.8	21.1	30.9	3.5	4.9	6.8	15.8

[a] Grafting conditions: [monomer] = 0.75 M; [HNO_3] = 0.1N.

mer (methyl acrylate) progressively reduces free diffusion, an attempt was made to combine this effect with the simultaneous introduction of acid groups. Thus mixtures of acrylonitrile and acrylic acid were used as comonomers in the system paper–ceric ammonium nitrate–nitric acid. Various comonomer ratios at various graft levels were investigated, and the results are shown in Table II. These results show that at high AN:AA ratios the free diffusion rate is rapidly reduced to a very low level with increasing add-on, but the resistance of the membranes increases correspondingly since the polyacrylonitrile is, of course, nonconducting. The wet strength of all of the products appeared adequate, however, and the appropriate combination of reactants and conditions (e.g. 1:1 molar acrylonitrile:acrylic acid to ca. 30% add-on) appear to produce an acceptable semipermeable membrane.

The rate of polymerization of mixtures of acrylonitrile and acrylic acid on paper (Table II) is similar to that anticipated from experiments with the individual monomers (Fig. 3), but Table II shows that the ratio of polyacrylic acid to polyacrylonitrile in the grafted paper, decreases progressively with increasing graft level. This effect confirms the suggestion made above, that the restriction of rate of polymerization and of graft level with acrylic acid is probably associated with the presence of acidic groups in the substrate and their sorption of Ce^{4+} and/or Ce^{3+}. Such an effect would operate less effectively with polyacrylonitrile in the copolymerization.

The major disadvantages of the procedure described above (viz., graft copolymerization of acrylonitrile and acrylic acid on paper) are the slow rate of polymerization and the limitation on graft level (cf. Fig. 1). This disadvantage can be overcome by grafting mixtures of acrylonitrile and methyl acrylate on paper and subsequently saponifying the polymethylacrylate to polyacrylic acid. This procedure however, results in a membrane with a high free diffusion rate, since the interfiber pores are reopened by the saponification treatment. It is therefore necessary to crosslink the finished membranes as already described for papers.

The saponification treatment used in the experiments of Table III is relatively drastic in order to secure complete hydrolysis of inaccessible ester groups, and the reagent used (10% sodium hydroxide solution) would be expected to extract hemicelluloses from the paper, but we do not have any measure of the extent of such extractions in the present experiments.

The effect of crosslinking, as already demonstrated, is to reduce the swelling of the membrane in water and to reduce the free diffusion rate. The resistance is, however, simultaneously increased by crosslinking, since the conductivity of the uncrosslinked membrane is in part due to diffusion of anions as well as cations.

The results in Table III show that the polyacrylonitrile content of the saponified membranes increases with graft level as would be anticipated, whereas the polyacrylic acid content remains approximately constant.

TABLE III
Membranes from Graft Polymerization of Acrylonitrile–Methyl Acrylate Mixtures on Paper, with Subsequent Saponification[a]

	AN:MA molar ratio = 2:1			AN:MA molar ratio = 1:1	
	5 min.	15 min.	30 min.	5 min.	15 min.
ΔW, %[b]	42.5	65.5	91.6	60.0	121
N, %	4.4	5.7	6.4	3.80	5.86
Capacity, meq./g.					
Before crosslinking	1.67	1.36	1.66	2.87	—
After crosslinking	1.62	1.48	1.40	2.22	2.65
Acrylonitrile content, %	16.7	21.6	24.2	14.4	22.2
Acrylic acid content, %	12.0	9.8		20.7	19.1
Water uptake, %					
Before crosslinking	91	84	87	144	—
After crosslinking	88	77	74	129	124
Free diffusion $\times 10^6$, meq./cm.^{2} sec.					
Before crosslinking	32.5	20.5	7.15	54.4	19.0
After crosslinking	24.8	7.3	3.3	22.9	19.1
Resistance, ohm/cm.^{2}					
Before crosslinking	1.8	4.4	11.0	1.5	4.6
After crosslinking	5.6	6.5	16.2	3.4	8.6

[a] Grafting conditions: [monomer] = 0.75 M; [HNO_3] = 0.1N.
[b] Total add-on, before saponification (all other results are after saponification).

This fact might indicate the presence of ungrafted polyacrylic acid, but could also be explained by the selective extraction by the alkali of hemicelluloses originally grafted with relatively high proportions of the more reactive methyl acrylate.

Microanalyses were performed by Mr. A. T. Masters; we are grateful to Mr. N. Truscott and Mr. R. D. Ponchaud for experimental assistance.

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Synopsis

Polymerizations of acrylic acid, acrylonitrile, and methyl acrylate on parchmentized paper, initiated by ceric ion, have been shown to occur at very different rates. The retardation of polymerization with the first two monomers is probably due to sorption of Ce^{4+} and/or Ce^{3+} on the grafted paper. The rate of polymerization of acrylonitrile on paper as a function of sulfuric acid concentration has been shown to be a maximum at 0.25*N*. The grafted papers show negligible loss in weight when extracted with solvents for the (vinyl) homopolymer at 80°C. Grafted papers containing polyacrylic acid have been evaluated as permselective ion exchange membranes. The paper is initially permeable to both cations and anions in aqueous solution, but by graft polymerization of suitable monomers the interfiber pores are blocked, and the membrane is simultaneously rendered semipermeable. The blocking of the interfiber pores is favored by the use of a nonhydrophylic comonomer, e.g. acrylonitrile, or by crosslinking, while the semipermeability is achieved by the use of acrylic acid itself or a suitable precursor such as methyl acrylate.

Résumé

On a démontré que des polymérisations d'acide acrylique, d'acrylonitrile et d'acrylate de méthyle initiées par l'ion cérique ont lieu sur du papier parcheminé, à des vitesses fort différentes les unes des autres. Le phénomène de retardement de la polymérisation des deux premiers monomères est probablement due a l'adsorption du Ce^{4+} et/ou Ce^{3+} sur le papier greffé. On a démontré que la vitesse de polymérisation de l'acrylonitrile sur papier en fonction de la concentration en acide sulfurique atteint un maximum à 0.25*N*. Les papiers greffés ne subissent qu'une perte négligeable en poids après extraction par solvants, de l'homopolymère (vinylique) à 80°C. On a déterminé la valeur des membranes permsélectives échangeuses d'ions que constituent les papiers greffés contenant de l'acide polyacrylique. Initialement le papier est perméable tant aux cations qu'aux anions en solution aqueuse, mais lors de l polymérisation greffée à l'aide de monomère adéquats les pores entre les fibres sont bloquées et en même temps la membrane devient semiperméable. Le bloquage des pores est favorisé par l'usage d'un comonomère non-hydrophile (p.ex. l'acrylonitrile) ou par pontage, tandis que la semiperméabilité est obtenue en faisant usage de l'acide acrylique lui-même, ou d'un précurseur adéquat tel que l'acrylate de méthyle.

Zusammenfassung

Es wurde gezeigt, dass die durch Ceriionen gestartete Polymerisation von Acrylsäure, Acrylnitril und Methylacrylat auf pergamentisiertem Papier mit sehr unterschiedlicher

Geschwindigkeit verläuft. Die Verzögerung der Polymerisation bei den beiden letzteren Monomeren wird wahrscheinlich durch Sorption von Ce^{4+} und Ce^{3+} am aufgepfropftem Papier verursacht. Die Polymerisationsgeschwindigkeit von Acrylnitril auf Papier besitzt in Abhängigkeit von der Schwefelsäurekonzentration ein Maximum bei 0,25*N*. Das aufgepfropfte Papier zeigt bei Extraktion mit Lösungsmitteln für das Vinyl-Homopolymere bei 80°C einen vernachlässigbaren Gewichtsverlust. Mit Polyacrylsäure aufgepfropftes Papier wurde auf seine Verwendbarkeit als permselektive Ionenaustauschmembrane überprüft. Das Papier ist ursprünglich für Kationen und Anionen in wässriger Lösung durchlässig, durch Pfropfpolymerisation geeigneter Monomerer werden aber die interfibrillären Poren blockiert und die Membrane gleichzeitig semipermeable gemacht. Die Blockierung der interfibrillären Poren wird durch die Verwendung eines nicht-hydrophilen Comonomeren (Z.B. Acrylnitril) oder durch Vernetzung begünstigt, während Halbdurchlässigkeit durch Verwendung von Acrylsäure selbst oder eines geeigneten Präcursors wie Methylmethacrylat erreicht wird.

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Polymerization Under Conditions of Rapid Decomposition of the Initiator

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INTRODUCTION

Classical radical polymerization is characterized by an arrangement in which the concentration of the initiator and thus also the quantity R_i remains constant in the course of the polymerization. The polymerization has a steady-state character making possible the quantitative investigation of various dependencies. According to the type of the initiator employed the polymerization has to be kept at such a temperature at which its decomposition takes place at the required rate. The total quantity of catalyst decomposed during the polymerization may not exceed several per cent if the above-mentioned dependencies are to be valid. The polymerization rates are, under these conditions, limited to a certain maximum above which the polymerization is accelerated as a result of insufficient transfer of heat.

If we increase the temperature of the polymerization we reach a region where the usual square-root dependence does not hold because the concentration of the initiator decreases in the course of the polymerization. By a further rise of temperature we finally arrive at a region where the initiator (at a suitable concentration) is decomposed before a higher conversion is reached. The unstationary state is here distributed throughout the period, which corresponds to the total decomposition of the initiator. As regards kinetics, the stated course may be expressed by the equation:

$$\frac{dR}{dt} = [\mathrm{I}_0]e^{-k}dt - ktR^2$$

under the assumption that termination is a normal combination of the growing chains and that the efficiency of initiation is 1. The solution of this differential equation, suitable for numerical evaluation, was found by Chien[1] and Magat.[2]

The polymerization generally must be carried out at temperature as low as possible if the transfer constants are not to attain high values. Therefore it cannot be effected under the stated conditions with usual initiators. One of the authors[3] investigated the relations between the structure of the

initiators and their decomposition rates with regard to low-temperature initiators together with a kinetic discussion of unstationary states.

Hyponitric acid esters, azo-α,α'-phenylpropionitrile, 3,6-dimethyl-3,6 dicyano-3,4,5,6 tetrahydropyridazine and benzenesulfonyl peroxide, possibly other peroxides as well seemed to have decomposition rates suitable for polymerization carried out under the conditions of a rapid consumption of the catalyst. We have investigated the hyponitric acid esters in detail.[4] Besides hyponitrites we used also the other substances (with the exception of benzenesulfonyl peroxide) for comparison in this paper.

Polymerizations can be perfectly controlled in a very narrow temperature range at such a temperature at which the initiator decomposes in the course of several minutes. In case the feeding of the initiator is controlled by the chosen temperature, the feeding is interrupted after reaching this value and started again after a decrease of temperature. Accumulation of the initiator (and thus an uncontrolled polymerization) cannot take place. The top limit temperature of this type of polymerization is that temperature at which the initiator, after being injected, cannot dissipate uniformly in the solution prior to its partial decomposition.

EXPERIMENTAL

A. Materials

1. Methyl Methacrylate. Methyl methacrylate was purified by double distillation on a 20-plate column under reduced pressure. The purity was controlled by gas chromatography. Acrylonitrile was purified in a similar manner.

2. *n*-Hexadecane. *n*-Hexadecane was prepared by the hydrogenation of *n*-hexadecyl alcohol, which was purified by distillation. The purity was controlled chromatographically.

3. Bis(cetyl Hyponitrite). Bis(cetyl hyponitrite) was prepared by shaking of an ethereal solution of *n*-hexadecyl iodide with silver hyponitrite in a 1:1 molar ratio for 48 hr.[5] After filtering off the AgI, the ether was evaporated in vacuum and the crude product repeatedly crystallized from petroleum ether by dissolving it at room temperature and cooling (m.p. 56.6°C.). The rate of decomposition k_d was determined from the quantity of nitrogen evolved[4] as:

$$k_{d_{70}} = 1.08 \times 10^{-3} \text{ sec.}^{-1}$$

$$k_{d_{80}} = 3.43 \times 10^{-3} \text{ sec.}^{-1}$$

4. 3,6-Dimethyl-3,6-dicyano-3,4,5,6-tetrahydropyridazine. 3,6-Dimethyl-3,6-dicyano-3,4,5,6-tetrahydropyridazine[3] was prepared by the bromine oxidation of the hydrazo compound in an aqueous alcoholic solution acidified with HCl at −40°C. The product was isolated by pouring the reaction mixture into ice water with subsequent rapid suction filtration.

The crude product was twice crystallized by dissolving in toluene at −10°C. with subsequent addition of petroleum ether and cooling. The substance forms pale yellow crystals which violently decompose over 0°C. The decomposition rate was determined from the quantity of the N_2 evolved as

$$k_{d_{15}} = 2.64 \times 10^{-3} \text{ sec.}^{-1}$$

5. Azo-2,2-bisphenylpropionitrile. Azo-2,2-bisphenylpropionitrile was prepared from acetophenone azine by the reaction with HCN. The resulting hydrazo compound was recrystallized several times from EtOH, suspended in diluted HCl (3:2) and oxidized by chlorine. The product was twice crystallized from ether by dissolving at 0°C. and cooling. The decompositiyn rate was determined from the quantity of N_2 evolved as[3,7]

$$k_{d_{30}} = 7.16 \times 10^{-3} \text{ sec.}^{-1}$$

B. Apparatus and Experimental Arrangement

The polymerizations were carried out in 250 ml. flasks schematically shown in Figure 1. The flask was equipped with a ground glass mercury-seal stirrer fitted with a receiver for released grease. One side arm was closed by a special stopper with acrylonitrile rubber gasket constructed for feeding of the initiator by means of a hypodermic syringe, the second one was closed with a three-way stopcock sealed at its end.

The flask was further equipped with a tube for the insertion of a battery of thermocouples (ten Cu–constantan couples). Oxygen was removed by repeating several times the cycle of cooling (liquid N_2), evacuation to less than 10^{-4} mm. Hg, filling with purified nitrogen, and heating to room temperature. In the course of the evacuation of the flask with monomer, one of the two side arms was connected to the vacuum, the second one to the central neck so that the space over the stirrer and in the flask were under the same pressure during evacuation. After eliminating the oxygen, the connecting piece was removed and the flask immersed in the thermostat, where it was heated to constant temperature at a constant stirring speed. The polymerization was started by setting the feeding apparatus into operation. The initiator solution was injected by means of the hypodermic syringe, the needle of which passed just through the stopper, so as not to touch its metal wall, thus avoiding premature decomposition. In the course of the feeding it is necessary to take care that the initiator dropped directly into the stirred liquid. Exact feeding by means of a hypodermic syringe required that the initiator solvent be a liquid of suitable viscosity. Because of the fact that majority of the polymerization experiments were precipitating polymerizations of methyl methacrylate in heptane, *n*-hexadecane was employed as the initiator solvent. This same solvent in a small quantity only was used also in the homogeneous polymerization experiments.

A smaller number of experiments was carried out under the same conditions, but with the application of a vibrating stirrer. There is no substantial difference between both methods of stirring in this case. The regulation of the feeding was carried out by means of a linear feeding apparatus controlled by an impulse compensation regulator (METRA type MuRis) in bridge connection. The linear feeding apparatus was coupled in its whole range with a variable resistance. The temperature in the flask as well as the quantity of the initiator injected were recorded potentiometrically. After

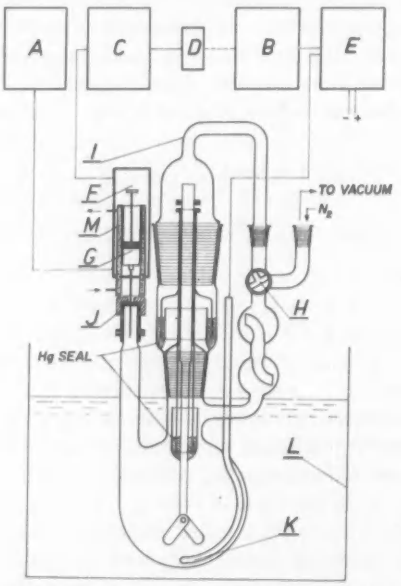

Fig. 1. Schematic diagram of the polymerization apparatus. (*A*) 2 mv. recorder (feeding); (*B*) 2 mv. recorder (temperature); (*C*) impulse compensation regulator; (*D*) resistance transmitter; (*E*) compensation voltage divider; (*F*) feeding apparatus; (*G*) hypodermic syringe; (*H*) three-way stopcock; (*I*) glass connecting piece; (*J*) special stopper; (*K*) thermobattery; (*L*) thermostat; (*M*) cooling jacket.

starting the feeding at the chosen rate, the initiator begins to decompose rapidly in the flask. The polymerization causes a rise of the temperature in the flask. Simultaneously, depending on the shape of the flask and other factors, a partial transfer of heat from the flask to the thermostat takes place. The rise of temperature is proportional to the rate of the feeding. At that moment when the temperature in the reaction vessel approaches the chosen limit (e.g., to 0.1°C.), the feeding is gradually slowed down and interrupted when the temperature limit is reached. The polymerization continues until the added initiator is decomposed. With the subsequent decrease of temperature below the chosen limit, reduced feeding is again put into operation, and with a further decrease full feeding is started.

The period of the cycle of switching off and on of the feeding depends on the conditions under which the polymerization is carried out. The period is, however, principally determined by the rate of feeding of the initiator. The length of the impulse is given in certain limits by the degree of unbalancing of the resistance bridge in the impulse compensation regulator. The frequency of the cycles was short enough to ensure continuous polymerization with exception of cases with high feeding rates. Linear continuous feeding occurs only if the temperature limit is sufficiently high not to be attained in the course of the whole feeding. In this case the polymerization is regulated by reduced feeding or not controlled at all. In the course of an uncontrolled polymerization an isothermic process is attained by sufficiently low feeding rate when the heat transfer is in equilibrium with heat of the polymerization reaction.

In case the feeding rate is high and the chosen limit low, the powerful impulses cause a sawlike course of the temperature in the flask.

Calibration of the flasks for the calculation of the conversion was carried out by recording the temperature at known values of the input of an auxiliary heater under the same conditions as in polymerization experiments and by calculation of the calorimetric constant.

The extent of the resulting conversion is proportional to the area limited by the course of the temperature during polymerization with the basic temperature. The feeding was interrupted after reaching the required conversion. The temperature gradually falls to its basic value proportionally to the consumption of initiator (if the tube for the battery of thermocouples is not coated by precipitated polymer or if the temperature equilibrium is not unbalanced by, e.g., a considerable change of viscosity of the polymerizing mixture).

The polymers were precipitated by pouring into methyl alcohol, dried, and weighed. The agreement with the calculated conversions reached 2–4% with the exception of experiments involving one of the above-mentioned difficulties.

RESULTS

Examples of the course of uncontrolled precipitation polymerizations are shown in Figures 2 and 3 and Tables I and II. Uncontrolled homogeneous polymerization would require a temperature limit higher than several tenths of one degree Centigrade and therefore were not carried out. After starting the feeding the temperature in the flask rises continuously and proportionally to concentration R_i until the moment of interruption (possibly, it continues at lower decomposition rates for a short time after interruption). The temperature then falls to the basic value in a period which agrees with the quantitative decomposition of the remaining initiator.

The initial course of controlled polymerization (Fig. 4 and Table III) is identical with the course of uncontrolled polymerizations. From the moment of control, however, the polymerization is regulated and has an iso-

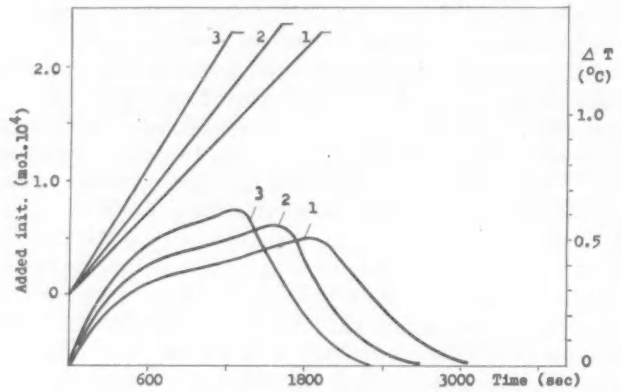

Fig. 2. Uncontrolled heterogeneous polymerization of MMA at 80°C. in heptane solution initiated by cetyl hyponitrite at various rates of feeding: (*1*) 0.3 ml./min.; (*2*) 0.4 ml./min.; (*3*) 0.5 ml./min.

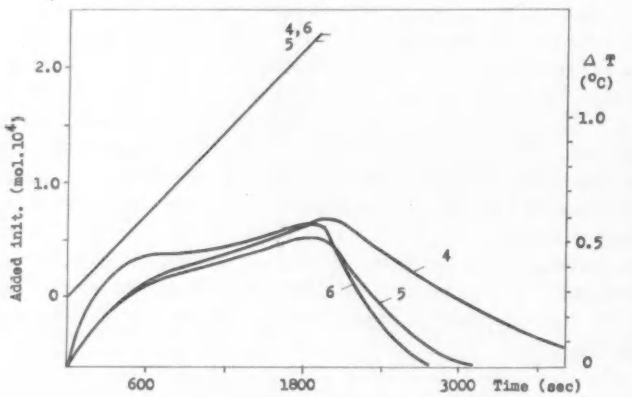

Fig. 3. Dependence of uncontrolled heterogeneous polymerization of MMA in heptane solution initiated by cetyl hyponitrite on basic temperature: (*4*) 76°C.; (*5*) 82°C.; (*6*) 86°C.

TABLE I
Uncontrolled Heterogeneous Polymerization of MMA with Hyponitrite Initiator, Heptane Solvent

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. × 10^2	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio, P/I
1	80	Unlimited	2.32	3.42	0.3	233.40
2	80	Unlimited	2.32	3.41	0.4	240.65
3	80	Unlimited	2.31	4.41	0.5	273.64

TABLE II
Dependence of Uncontrolled Heterogeneous Polymerization of MMA on Temperature with Hyponitrite Initiator, Heptane Solvent

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. $\times 10^2$	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio, P/I
4	76	Unlimited	2.31	3.40	0.3	345.76
5	82	Unlimited	2.32	3.32	0.3	233.40
6	86	Unlimited	2.31	3.44	0.3	228.04

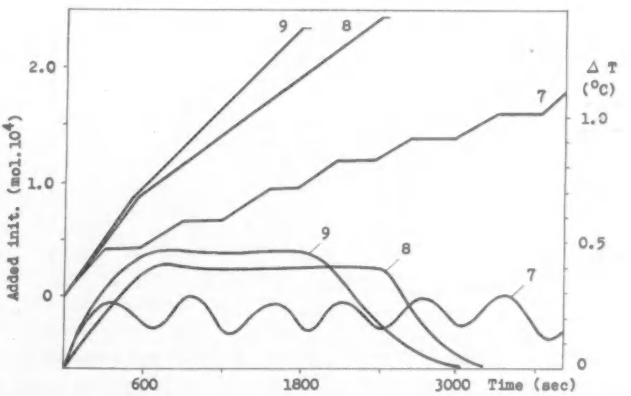

Fig. 4. Dependence of controlled heterogeneous polymerization of MMA in heptane solution initiated by cetyl hyponitrite at a basic temperature of 80°C., and constant feeding rate on temperature limit: (7) 0.24°C.; (8) 0.35°C.; (9) 0.59°C.

thermic course. After the interruption of the initiator feed the course of the polymerizations becomes again comparable to the preceding ones with the exception of the sawlike course (Fig. 4, curve 7). The polymerization in this last case reached high conversions with a smaller consumption of the initiator than in the preceeding two cases.

The influence of temperature was studied on homogeneous and heterogeneous polymerizations of methyl methacrylate initiated by hyponitrite in the 76–86 ±0.02°C. range. It is shown that the sawlike course is charac-

TABLE III
Dependence of Controlled Heterogeneous Polymerization of MMA on Temperature Limit with Hyponitrite Initiator, Heptane Solvent

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. $\times 10^2$	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio P/I
7	80	0.24	2.32	3.45	0.5	1204.13
8	80	0.35	2.32	3.53	0.5	307.59
9	80	0.59	2.32	3.42	0.5	273.39

teristic for low temperature limit in the temperature range studied. The time necessary for the 95% decomposition of the initiator at these temperatures varies from 20 to 7 min. The results, shown in Figures 5 and 6 and Tables IV and V, indicate a considerable dependence on temperature. The molar ratio of polymer/initiator as a function of temperature for a homogeneous methyl methacrylate polymerization is illustrated in Figure 7. The ratio decreases rapidly with increasing temperature. The results for heterogeneous polymerizations cannot be compared, as in this latter case some of

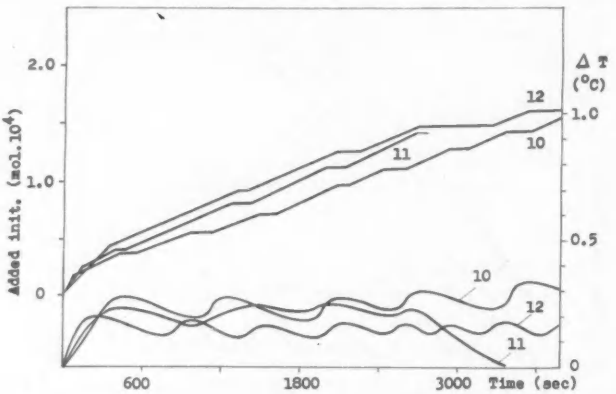

Fig. 5. Dependence of controlled heterogeneous polymerization of MMA initiated by cetyl hyponitrite with low temperature limit on heptane solution, on basic temperature: (*10*) 76°C.; (*11*) 82°C.; (*12*) 86°C.

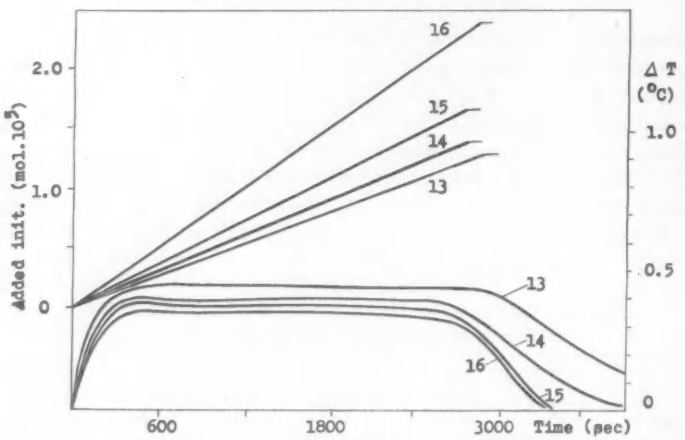

Fig. 6. Temperature dependence of controlled homogeneous polymerization of MMA initiated by cetyl hyponitrite: (*13*) 76°C.; (*14*) 80°C.; (*15*) 82°C.; (*16*) 86°C.

TABLE IV
Dependence of Controlled Heterogeneous Polymerization of MMA with Low Temperature Limit on Basic Temperature with Hyponitrite Initiator, Heptane Solvent

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. $\times 10^2$	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio P/I
10	76	0.24	2.31	3.42	0.3	1324.14
11	82	0.24	2.32	3.44	0.3	383.68
12	86	0.24	2.31	3.43	0.3	773.64

TABLE V
Dependence of Controlled Homogeneous Polymerization of MMA on Temperature with Hyponitrite Initiator

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. $\times 10^2$	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio, P/I
13	76	0.47	1.19	9.34	0.05	6446.9
14	80	0.47	1.16	9.34	0.05	6202.6
15	82	0.47	1.16	9.34	0.05	5858.4
16	86	0.47	1.16	9.34	0.05	4307.6

the polymerizations take a sawlike course. With a temperature higher than 86°C. the polymerization has an irregular course.

The lower controllable limit is a temperature of approximately 70°C.

The relation between the quantity of initiator consumed and the quantity of polymer obtained by controlled polymerization at constant basic tem-

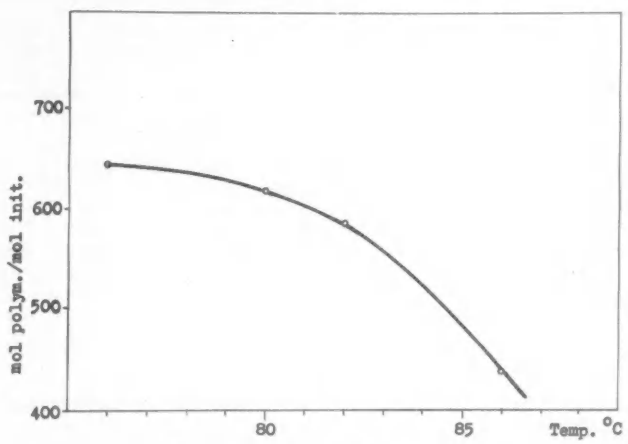

Fig. 7. Dependence of the molar ratio of polymer to initiator (P/I) on temperature for a homogeneous methyl methacrylate polymerization initiated by cetyl hyponitrite.

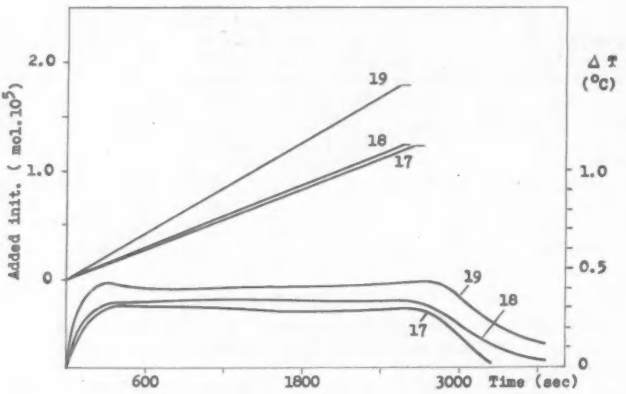

Fig. 8. Dependence of controlled homogeneous polymerization of MMA at 80°C. initiated by cetyl hyponitrite on concentration of the initiator: (*17*) 0.0054 mole/l.; (*18*) 0.0116 mole/l.; (*19*) 0.0232 mole/l.

perature is shown in Figure 8 and Table VI. In the given feeding range, the difference between rapid and slow feeding (in the initial state) amounts to several per cent. As expected, the highest efficiency was obtained at the

TABLE VI
Dependence of Controlled Homogeneous Polymerization of MMA on Concentration of the Initiator with Hyponitrite Initiator

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. × 10^2	Monomer, mole/l.	Rate of feeding, ml./min	Molar ratio, P/I
17	80	0.47	0.54	9.34	0.05	6420.5
18	80	0.47	1.16	9.34	0.05	6202.6
19	80	0.47	2.32	9.34	0.05	6050.6

TABLE VII
Controlled Homogeneous Polymerization of MMA with Azophenylpropionitrile Initiator

Expt. no.	Temp., °C.	Temp. limit, °C.	Initiator, mole/l. × 10^2	Monomer, mole/l.	Rate of feeding, ml./min.	Molar ratio, P/I
20	35	0.47	4.33	9.34	0.3	111.76
21	30	0.47	4.33	9.34	0.3	155.04

slowest feeding rate. In case a gel effect occurs during polymerization the efficiency rises very considerably.

The results of the polymerization with phenyl azopropionitrile at 30 and 35°C. are given in Figure 9 and Table VII. Because of the great stability on the initiator radical it is possible to expect a low efficiency (it is indicated

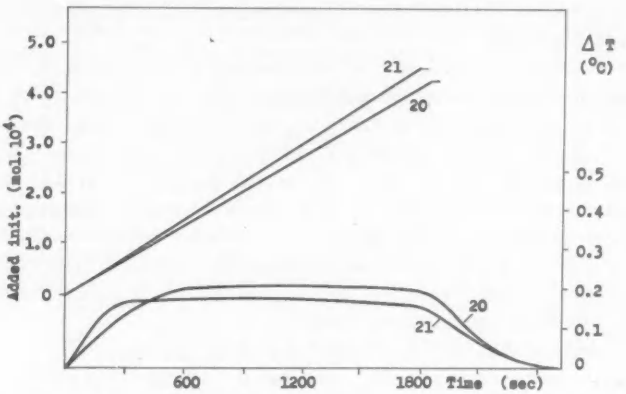

Fig. 9. Temperature dependence of controlled polymerization of MMA initiated by azo-2,2′-bisphenylpropionitrile: (*20*) 35°C.; (*21*) 30°C.

that phenylazopropionitrile is approximately 60 times less efficient than hyponitrite with respect to the ratio P/I).

As a further initiator 3,6-dimethyl-3,6-dicyanotetrahydropyridazine was used; for this initiator a similar reactivity as in the case of azonitrile was expected, though decreased by the easier possibility of a combination of growing chains.[6] However, under the conditions of rapid decomposition its efficiency is practically zero.

The acrylonitrile polymerization proceeds similarly as a precipitation heterogeneous methyl methacrylate polymerization. The higher heat of polymerization causes a greater variation of temperature in the controlled

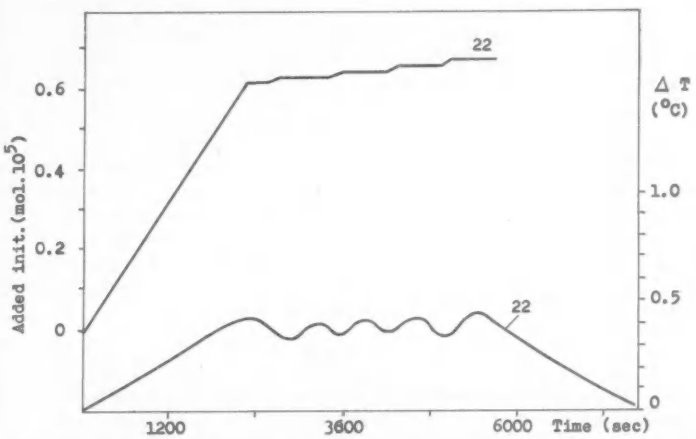

Fig. 10. Controlled polymerization of acrylonitrile at 72°C. initiated by cetyl hyponitrite.

state. A typical example of the controlled acrylonitrile polymerization is shown in Figure 10.

The described method of the polymerization has several advantages. The polymerization is started instantly as in the case of photopolymerization. The beginning and the end of the polymerization has an unstationary course in the required period depending on the temperature and the chosen limits. In a range less than 1°C., the rate of decomposition of the initiator remains practically constant. In the controlled state the quantity of added initiator corresponds to the quantity of initiator radicals in the system. The values of all variables can be continuously recorded. The quantity of the monomer is not limited by the requirement of an isothermic reaction as, e.g., in dilatometric experiments.

The consumption of the initiator should be approximately several per cent of the usual arrangement. The results indicate that such a level of consumption can be reached in the case of homogeneous as well as heterogeneous polymerizations. The steep rise of the temperature dependence of the molar ratio of polymer to initiator indicates that the partial decomposition of the initiator in the needle prior to its injection into the monomer has probably not yet been completely eliminated.

The arrangement allowed the preparation of the polymer isothermally with the temperature oscillating around the chosen value. The only variables of this arrangement were the temperature limit and feeding rate.

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Synopsis

The polymerization of methyl methacrylate and acrylonitrile has been studied in conditions of rapid catalyst consumption. The described experimental arrangement facilitated a controlled, automatically regulated polymerization in an adjustable temperature range. The conversion was determined from the polymerization heat. This arrangement makes possible a regular course of the polymerization. The consumption of the initiator is in best cases about by two orders lower than in usual arrangement. Fundamental parameters of this process were determined.

Résumé

On a étudié la polymérisation du méthacrylate de méthyle et de l'acrylonitrile dans des conditions d'une diminution rapide deconcentration en catalyseur. On a atteint grâce à une installation expérimentale décrite par ailleurs, un cours automatiquement règlé et enregistré dans des limites des températures ajustables. La conversion a été déterminée par mesure de la chaleur de polymérisation. Ce dispositif permet un cours

linéaire de la polymérisation. La quantité de l'initiateur consommé est dans les cas les meilleurs d'environ deux ordres de grandeur plus bas que dans le procédé usuel. On a déterminé les paramètres fondamentaux de ce procédé de polymérisation.

Zusammenfassung

Es wurde die Polymerisation von Methylmethacrylat und Acrylnitril bei schneller Abnahme der Katalysatorkonzentration untersucht. Mit der beschriebenen Versuchsanordnung kann in einem einstellbaren Temperaturbereich eine automatische Regulierung und Registrierung des Reaktionsverlaufes erreicht werden. Der Umsatz wurde mittels der Polymerisationswärme bestimmt. Die gewählte Anordnung ermöglicht einen linearen Polymerisationsverlauf. Die Menge des verbrauchten Starters ist in optimalen Fällen um zwei Grössenordnungen kleiner als bei der konventionellen Reaktionsführung. Es wurden die Grundparameter dieses Polymerisationsprozesses bestimmt.

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Quelques Exemples de Polymérisation en Phase Mésomorphe

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Depuis quelques années on s'est intéressé, dans divers laboratoires, à la polymérisation de monomères dans des conditions telles que les produits obtenus gardent en quelque sorte le "souvenir" du milieu dans lequel s'est déroulée la réaction de polymérisation. On espère ainsi conférer aux polymères des propriétés nouvelles, une régularité de chaîne plus grande, ou une anisotropie de forme qui résulterait de la symétrie de l'espace dans lequel s'est déroulée la réaction de polymérisation.[1]

Les travaux effectués jusqu'ici dans cette optique peuvent se classer en trois catégories: les polymérisations (*1*) à l'état solide de monomères cristallisés, (*2*) en insertion et (*3*) en couches adsorbées.

(*1*) Les polymérisations à l'état solide de monomères cristallisés: Dans ce domaine se sont illustrés Letort[2] et Morawetz[3] qui ont cherché le plus souvent à conférer ainsi au polymère la structure la plus régulière possible.

(*2*) Les polymérisations en insertion: Dans cette catégorie nous rangerons les travaux de Brown et White[4] sur la polymérisation de monomères inclus dans les "canaux" de l'urée ou de la thiourée. Ils ont pu obtenir ainsi des polymères stéréorégulièrs. De son côté Blumstein[5] a préparé des composés d'insertion de différents monomères polaires avec la montmorillonite. La polymérisation se déroule ici à l'intérieur des feuillets et on obtient des polymères très ramifiés, en "nappe."

(*3*) Les polymérisations en couches adsorbées:[6] Il a été possible de provoquer la polymérisation de monomères polaires adsorbés en couche monomoléculaire, à la surface de l'eau.

Les travaux dont nous rendons compte dans le présent mémoire ont pour objet l'étude de la polymérisation en milieu liquide cristallin. Ce sont les résultats obtenus, au cours des dernières années, par Luzzati et ses collaborateurs[7–17] qui ont suggéré cette technique de polymérisation. Ces chercheurs, en effet, ont établi la structure des phases mésomorphes qu'on rencontre dans les colloïdes d'association, et ont mis en évidence le fait remarquable qu'est la structure chaotique, quasi-liquide, des chaînes paraffiniques, dans ces édifices. Ces deux traits caractéristiques, organisation liquide-cristalline et état chaotique des chaînes hydrocarbonées, suggèrent la possibilité d'effectuer des polymérisations dans les gels méso-

morphes. Ceci peut être réalisé soit par polymérisation de monomères engagés dans la structure, donc en solution dans la partie paraffinique, soit par polymérisation de molécules ayant à la fois les propriétés de savon et de monomère, engagées dans des structures mésomorphes.

Le but recherché n'est pas ici d'obtenir des polymères doués d'une quelconque régularité structurale (tacticité) mais plutôt de figer des organisations particulières de régions paraffiniques et de couches polaires, et d'étudier les propriétés que cette organisation peut conférer au polymère.

Nous décrivons dans ce mémoire quelques exemples de polymérisation en phase mésomorphe, qui viennent compléter ceux qui ont déjà fait l'objet de publications.[18,19] Il convient de résumer brièvement les caractéristiques des principales phases mésomorphes qui interviennent dans ce travail.

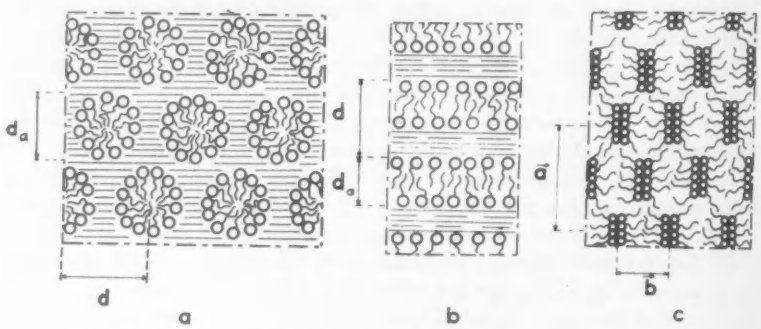

Fig. 1. Représentation schématique des structures: (*a*) phase médiane; (*b*) phase lisse; (*c*) phase en cylindres.

La phase lisse (Fig. 1*b*)[7–11] est constituée d'un empilement de doubles couches de savon et de feuillets d'eau. d_a et d_e sont respectivement les épaisseurs des feuillets de savon et d'eau; d est la période de la maille ($d = d_a + d_e$). d est une donnée de l'expérience; lorsque la concentration et le volume spécifique du savon sont connus on peut déterminer les valeurs de d_a et d_e.

La phase médiane (Fig. 1*a*)[7–11] est constituée par un assemblage hexagonal de cylindres de longueur indéfinie formés par les chaînes paraffiniques, et tapissés à leur surface par les groupes polaires. L'eau remplit l'espace entre les cylindres. La distance entre les axes des cylindres d est donnée par l'expérience; le calcul fournit les valeurs du diamètre des cylindres d_a.

La phase à rubans (Fig. 1*c*)[12–15] est formée d'un ensemble de cylindres indéfinis à section fortement anisodiamétrique ("rubans"), assemblés en réseaux bidimensionnels. Les groupes polaires sont disposés au centre des rubans, en double couche à structure très ordonnée. Les chaînes paraffiniques s'ouvrent en éventail, et remplissent l'espace entre les rubans.

Cette structure est caractérisée par les dimensions a et b de la maille rectangulaire centrée.

La phase en cylindres[16,17] dérive de la phase en rubans: la section des éléments de structure a ici une symétrie circulaire, et la maille est hexagonale.

Dans toutes ces structures les chaînes paraffiniques adoptent une configuration chaotique, plus voisine de celle d'une paraffine liquide que de l'organisation régulière d'un cristal de savon.[7-17] Lorsque les chaînes paraffiniques sont cristallisées, ce qui se produit en général à basse température et à faible teneur en solvant, on rencontre des structures tout-à-fait différentes dites "gels" ou "coagels" qui présentent peu d'intérêt pour la polymérisation.

En plus des paramètres définis ci-dessus, on utilise dans la suite la surface moyenne S dont dispose chaque groupe polaire à l'interface. On en détermine sans difficulté la valeur lorsque les dimensions des éléments de structure sont connues.

PARTIE EXPERIMENTALE

Les phases mésomorphes ont été caractérisées et étudiées au moyen du microscope polarisant et de la diffraction des rayons X, selon les techniques décrites ailleurs.[9]

Parmi les savons que nous avons utilisés, classés ici en trois groupes, nous citerons: (I) un mélange de savons de sodium de C_{12} à C_{18}, le myristate de Na, l'oléate de K, et l'undécylénate de K (tous produits commerciaux que nous avons purifiés); (II) les phényl stéarates de Na, K, Ca et les *p*-éthylphénylundécanoates de Na, K, Ca, Sr et Cd (que nous avons préparés au laboratoire par des méthodes originales qui seront décrites par ailleurs); (III) les *p*-styryl 10- et 11-undécanoates de Na, K, Ca (savons-monomères que nous avons préparés et purifiés au laboratoire en nous inspirant d'une méthode due à Freedman, Mason et Medalia[20]).

La polymérisation a été effectuée, selon les cas, à chaud (80–90°C) ou à température ordinaire, l'initiation étant assurée soit thermiquement, soit par irradiation ultra-violette, soit par action de promoteurs hydrosolubles tels que $S_2O_8K_2$, soit par action de catalyseurs organosolubles tels que l'azobisisobutyronitrile. Ce dernier produit peut jouer également le rôle de photosensibilisateur dans les polymérisations initiées par irradiation ultraviolette. On a pris soin de pousser les polymérisations à des taux de conversion élevés.

Dans tous nos diagrammes les concentrations sont exprimées en grammes de savon par gramme de mélange.

RÉSULTATS EXPÉRIMENTAUX

Nous examinerons successivement les résultats de la polymérisation de monomères en système ternaire (savon–eau–monomère) puis en système

binaire (savon–monomère) et enfin les résultats de la polymérisation des savons vinyliques eux-mêmes.

I. Polymérisation en Phase Ternaire Savon–Eau–Monomère

Nous avons utilisé ici exclusivement les savons du groupe I et nous sommes partis des structures connues et bien définies de leurs systèmes binaires savon–eau. La concentration du savon est de l'ordre de $c = 0{,}70$ pour la phase lisse et d'environ $c = 0{,}35$ pour la phase médiane. Nous avons introduit dans ces phases des quantités déterminées des monomères suivants: styrolène (additionné ou non de faibles quantités de divinylbenzène), isoprène et diméthylbutadiène. Ces monomères s'insèrent dans la couche paraffinique et "gonflent" la structure sans la détruire. Les concentrations en monomère utilisées étaient situées dans les limites de 0–20% par rapport au total savon + eau dans le cas du lisse, et de 0–10% dans le cas de la phase médiane.

L'étude aux rayons X des mélanges mésomorphes montre, dans tous les cas, que les paramètres structraux évoluent en cours de polymérisation jusqu'à atteindre les valeurs relatives aux mélanges savon–eau dépourvus de monomère. Les conditions de température et de concentration, le mode d'initiation, la nature des savons et des monomères utilisés importent peu. L'expulsion du polymère de la structure mésomorphe est un phénomène tout à fait général dans le cas de ces systèmes ternaires.

Remarquons que les échantillons, qui sont initialement homogènes et transparents, deviennent troubles au cours de la polymérisation. Les particules de polystyrolène réticulé extraites de la phase médiane ou de la phase lisse ont été examinées au microscope électronique. Elles ne présentent aucune morphologie particulière pouvant se rapporter au milieu dans lequel était censée se dérouler la polymérisation.

Nous avons effectué une étude physicochimique sur un polystyrolène non réticulé, préparé en phase lisse. Le produit a été fractionné et soumis à des mesures de diffusion de la lumière et de viscosité, en solution dans le benzène. La loi de viscosité que nous avons trouvée:

$$[\eta] = 2{,}29 \times 10^{-2} M^{0{,}66}$$

est comparable à celle obtenue sur des polystyrolènes préparés par les méthodes classiques. Le polymère est très polydisperse et contient une proportion importante de molécules de grande masse moléculaire. La température de polymérisation était élevée et la concentration en catalyseur importante; aussi cette prédominance des fortes masses, que nous avons retrouvée dans bien d'autres cas, ne peut-elle s'expliquer que par des taux de recombinaison des radicaux de polymère considérablement plus faibles que dans les polymérisations en solution. Ce caractère se retrouve dans les polymères préparés en émulsion.

Cette étude nous a donc conduit aux résultats suivants. (*1*) Il y a démixtion entre le polymère formé et la phase mésomorphe. (*2*) Les polymères obtenus ne gardent aucun "souvenir" du milieu mésomorphe

dans lequel était censée se dérouler la polymérisation. (*3*) La polymérisation dans les systèmes mésomorphes aqueux conduit, comme les polymérisations en émulsion, à des produits de masse moyenne et de polydispersité élevées.

II. Polymérisations de Monomères en Phase Binaire Savon–Monomère

Dans les phases aqueuses ternaires que nous venons de considérer, les molécules de savon, comme celles du monomère, jouissent d'une mobilité relativement grande qui peut favoriser la démixtion observée au cours de la polymérisation. Dans les gels mésomorphes binaires savon–hydrocarbure (resp. monomère), cette mobilité est considérablement réduite. Dans les phases à rubans ou à cylindres les groupes polaires sont figés en un assemblage compact. S'il est possible d'introduire un monomère dans la partie paraffinique d'une tel milieu, on peut donc espérer figer la structure mésomorphe par polymérisation du monomère inclus.

Les savons linéaires ne présentent des gels anisotropes qu'à des températures supérieures à 100–120°C. C'est pour quoi nous avons préparé des savons (groupe II) dont la chaîne paraffinique n'est pas linéaire. L'élément de désordre ainsi introduit abaisse la température de "fusion" des chaînes hydrocarbonées et facilite l'apparition de structures liquides cristallines.

Nous avons donc étudié les phases mésomorphes que présentent à l'état pur et à température ordinaire les savons suivants: *p*-éthylphényl-undécanoates (PEPU) de Na, K, Ca, Sr et Cd, phénylstéarates de Na, K et Ca, ainsi que leurs mélanges avec les deux monomères suivants: styrolène et méthacrylate de méthyle. Parmi tous ces systèmes nous n'avons retenu que ceux dans lesquels apparaissent des phases mésomorphes bien définies et qui présentent une variation nette de leurs paramètres structuraux avec la concentration en monomère. Ces systèmes sont les suivants: (I) phénylstéarate de Ca–styrolène (cylindres); (II) phénylstéarate de Ca–méthacrylate de méthyle (cylindres); (III) PEPU K–styrolène (rubans); (IV) PEPU Na–styrolène (rubans); (V) PEPU Ca–méthacrylate de méthyle (cylindres).

La polymérisation du mélange I entraîne une variation importante du paramètre structural qui retrouve finalement sa valeur relative au détergent pur. Ceci indique que le polymère se trouve expulsé de la phase mésomorphe au fur et à mesure de sa formation. Les échantillons deviennent troubles au cours de la polymérisation, indice d'une démixtion.

Dans le cas des mélanges II et V l'aspect du produit ne change pas au cours de la polymérisation. La variation des paramètres structuraux au cours de la polymérisation est faible mais il faut signaler que la variation de ces mêmes paramètres en fonction de la concentration du monomère avant polymérisation est peu importante également. La précision insuffisante des mesures ne permet pas de tirer de conclusion sur la localisation du polymère.

Dans le cas des mélanges III et IV il nous faut distinguer deux cas. (*a*) Si la concentration en monomère inclus est inférieure à 15–20% la polymérisation de celui-ci n'entraîne aucune variation des paramètres structuraux. Le polymère n'est donc pas expulsé de la phase. (*b*) Si la concentration en monomère dépasse 15–20% une partie du polymère formé au cours de la polymérisation entre en démixtion. La concentration de polymère maintenu dans la phase est de l'ordre de 15–à 20%. Sur les Figures 2–6 nous avons porté la variation des espacements réci-

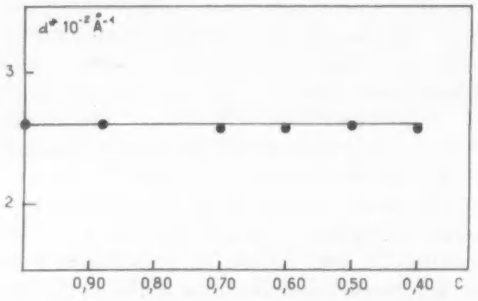

Fig. 2. Variation des espacements réciproques d^* en fonction de la concentration pour le système binaire phénylstéarate de Na–styrolène.

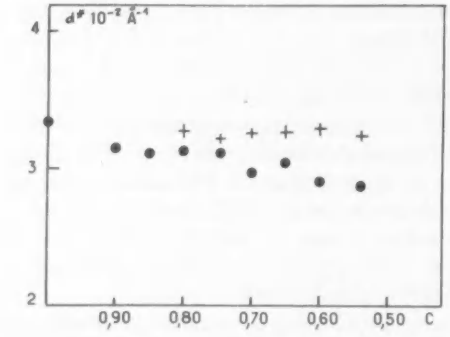

Fig. 3. Variation des espacements réciproques d^* en fonction de la concentration: (●) du système binaire phénylstéarate de Ca–styrolène; (+) du système binaire phénylstéarate de Ca–styrolène après polymérisation du monomère inclus.

proques, correspondants à la première raie de diffraction, en fonction de la composition des mélanges. Les diagrammes correspondants au savon + monomère (points noirs) y sont portés en même temps que ceux relatifs au système savon–polymère (croix). Nos figures illustrent les quatre cas possibles, à savoir: (*1*) démixtion dans le diagramme savon–monomère (Fig. 2); (*2*) mélange homogène savon–monomère, mais démixtion entre savon et polymère (Fig. 3); (*3*) phase homogène savon–monomère et phase

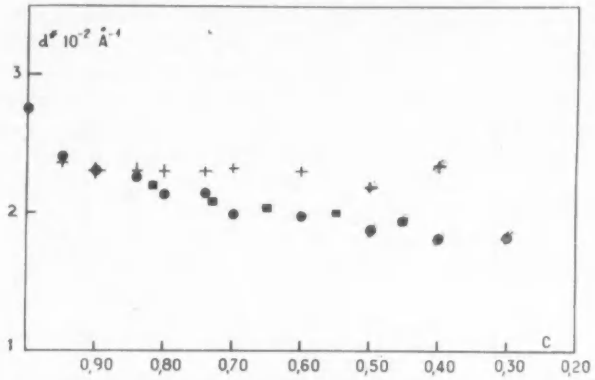

Fig. 4. Variation des espacements réciproques en fonction de la concentration: (●) du système *p*-éthylphénylundécanoate de K–styrolène; (+) du système *p*-éthylphénylundécanoate de K–styrolène après polymérisation du monomère inclus; (■) du système *p*-éthylphénylundécanoate de K–éthylbenzène. Les six points à droite du diagramme correspondant à des raies de diffraction floues.

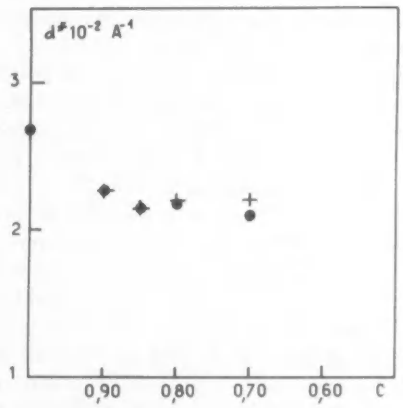

Fig. 5. Variation des espacements réciproques en fonction de la concentration: (●) du système *p*-éthylphénylundécanoate de Na–styrolène; (+) du système *p*-éthylphénylundécanoate de Na–styrolène après polymérisation du monomère inclus.

homogène savon–polymère jusqu'à une teneur limite en polymère (Figs. 4 et 5); (*4*) la Figure 6 illustre le cas où la précision insuffisante des résultats ne permet pas de tirer des conclusions définitives.

Nous pouvons donc affirmer que dans deux cas au moins le styrolène inclus dans la phase mésomorphe s'y polymérise sans en altérer la structure et sans en être expulsé.

L'addition au monomère de 20% de divinylbenzène devait permettre la réticulation du polymère dans la phase. Ce dernier, après que le savon

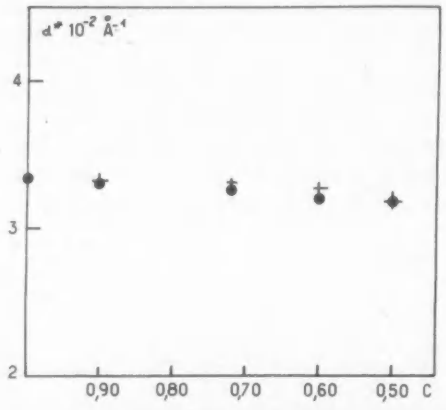

Fig. 6. Variation des espacements réciproques en fonction de la concentration: (●) du système phénylstéarate de Ca–méthacrylate de méthyle; (+) du système phénylstéarate de Ca–méthacrylate de méthyle après polymérisation du monomère inclus.

ait été extrait par le méthanol, se présente sous la forme d'une poudre blanche, insoluble, infusible dont le spectre d'absorption infra-rouge ne présente aucune particularité remarquable.

Examinés au microscope polarisant, les grains de polymère apparaissent fortement biréfringents. Lorsque le produit est gonflé par un liquide d'indice élevé, tel que l'acide dichloracétique, l'aspect des particules rappelle celui d'un gel mésomorphe. La biréfringence du polymère diminue quand on le chauffe et disparaît vers 115°C. Elle ne réapparaît pas quand on laisse refroidir l'échantillon, mais elle se manifeste à nouveau, de façon attenuée si on ajoute une trace d'acide dichloracétique.

L'examen aux rayons X du polymère obtenu indique une structure amorphe. On décèle, en revanche, une très forte diffusion centrale qui est due à la porosité des particules.

Il n'a donc pas été possible de mettre en évidence une structure particulière du polymère, que l'on puisse mettre en relation avec celle du gel mésomorphe dans lequel il s'est formé. La biréfringence de ces échantillons peut être attribuée à la forme des grains de polymère, ou bien à la présence de tensions, provoquées par l'élimination du savon qui constituait le support du système.

III. Polymérisation de Savons Vinyliques

Dans cette dernière partie nous examinerons le cas où le savon est en même temps un monomère vinylique. Le système mésomorphe formé par le savon pur ou en mélange binaire avec l'eau ne joue pas ici le rôle d'un moule moléculaire. C'est la polymérisation du savon, par son extrémité vinylique, qui est susceptible de rigidifier l'organisation du système. La polymérisation d'un tel savon, en présence de réticulant,

doit permettre de figer la structure mésomorphe et d'obtenir un polymère "organisé" conservant les propriétés optiques et cristallographiques du gel initial. Bien que ce procédé de polymérisation présente des analogies avec la polymérisation à l'état cristallin, il convient de souligner deux différences notables: l'organisation des molécules qui portent les groupements vinyliques est bidimensionnelle et les chaînes hydrocarbonées sont à l'état liquide.

Les savons que nous avons utilisés dans cette étude, dérivent des acides 10- et 11-styrylundécanoïques. Nous examinerons d'abord les résultats obtenus dans les systèmes binaires savon-eau, pour évoquer ensuite brièvement le cas des savons purs.

1. Systèmes Binaires

a. Structure des Gels. Dans chaque cas nous avons établi le domaine d'existence des différentes phases, nous en avons déterminé la structure et nous avons calculé les dimensions des différents éléments de structure.

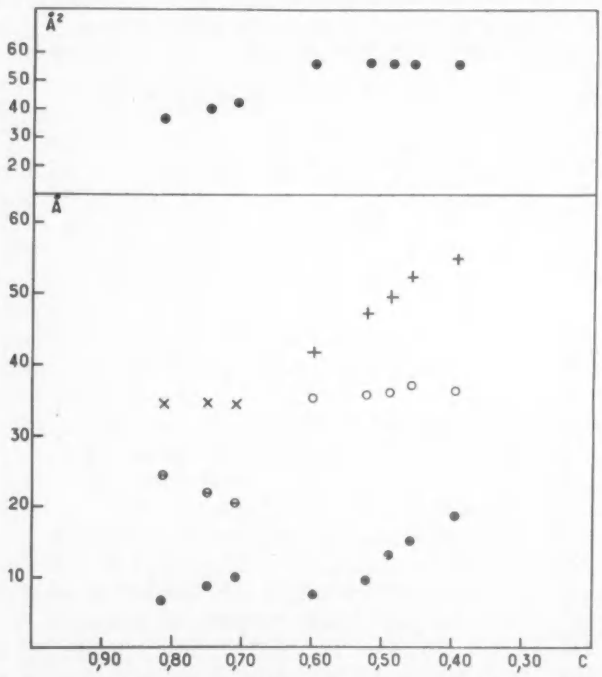

Fig. 7. Variation des dimensions des éléments de structure des phases médiane et lisse en fonction de la concentration du système 11-styrylundécanoate de Na–eau à 117°C. Phase médiane (+) distance entre cylindres d; (O) diamètre des cylindres de savon d_α. Phase lisse (×) équidistance entre feuillets d; (⊖) épaisseur des feuillets de savon d_a; (⊕) épaisseur des couches d'eau d_e; (●) surface disponible en moyenne par groupe hydrophile à l'interface savon–eau S.

Le 11-styrylundécanoate de sodium ne donne des phases mésomorphes qu'au dessus de 107°C. Nous avons pu identifier à 117°C une phase lisse et une phase médiane séparées par un domaine étroit de concentration que nous n'avons pas exploré avec soin (aux environs de $c = 0{,}60$). Le coagel apparaît pour des concentrations supérieures à $c = 0{,}85$. Les valeurs des paramètres structuraux sont représentées sur la Figure 7 en fonction de la composition du gel. Nous retrouvons là le comportement habituel des savons alcalins.

Le 11-styrylundécanoate de potassium donne des phases mésomorphes dès 70°C. Nous n'avons pu identifier qu'une structure unique, le médian, dont le domaine d'existence s'étend de $c = 0{,}35$ à $c = 0{,}70$. Si la concentration est supérieure à $c = 0{,}70$, le coagel apparaît.

Les 10-styrylundécanoates de potassium et de sodium présentent, eux, des phases mésomorphes dès la température ordinaire, ce qui semble être dû à la structure ramifiée de leur chaîne hydrocarbonée. Nous avons dû rejeter le savon de sodium en raison de la présence, sur les diagrammes de diffraction, de raies parasites dont nous n'avons pu déterminer l'origine

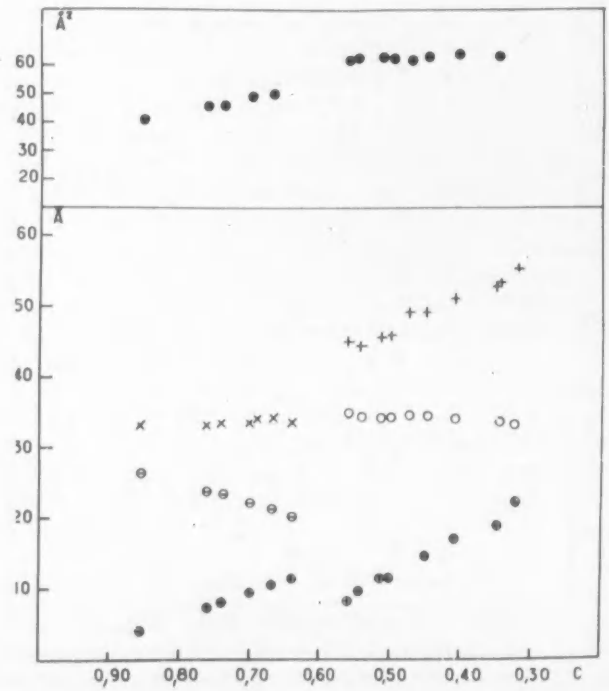

Fig. 8. Variation des éléments de structure des phases médiane et lisse, en fonction de la concentration du système 10-styrylundécanoate de K–eau à 22°C. (symboles cf. Fig. 7).

avec certitude. Le savon de potassium en revanche permet l'obtention des phases lisse et médiane bien définies à température ordinaire dans un domaine de concentration compris entre $c = 0{,}30$ et $c = 0{,}90$. La transition entre les domaines d'existence du lisse et du médian se situe aux environs de $c = 0{,}60$. La Figure 8 représente la variation des différents paramètres structuraux en fonction de la concentration en savon.

b. Etude de la Polymérisation en Milieu Mésomorphe. Le 11-styryl-undécanoate de sodium a été polymérisé à 117°C en phase lisse ($c = 0{,}70$) et en phase médiane ($c = 0{,}50$) en présence de faibles quantités de divinylbenzène. L'initiateur choisi était le peroxyde de ditertiobutyle, soluble en phase paraffinique. Comme le monomère est soluble dans le méthanol à chaud, alors que le polymère ne l'est pas, une détermination rapide du taux de conversion est possible. L'examen aux rayons X de nos échantillons montre que la structure de la phase n'est pas altérée par la polymérisation du savon. Les raies de diffraction caractéristiques de la phase initiale subsistent. La polymérisation s'accompagne cependant d'une faible dilatation du réseau (environ 10%). Quand la vitesse de polymérisation est faible, les raies de diffraction sont fines, ce qui indique une bonne organisation du milieu. Le gel polymérisé à 117°C conserve à température ordinaire la structure mésomorphe alors que, dans ces mêmes conditions, le mélange monomère-eau se présente sous la forme d'un coagel.

Nous avons effectué la polymérisation du 11-styrylundécanoate de potassium à 70°C en présence de divinylbenzène comme réticulant. Bien que nous ayons opéré ici dans des conditions plus douces que dans le cas précédent, la structure médiane que présente ce savon en milieu aqueux semble plus fragile que ne le sont celles de l'homologue sodique. La meilleure organisation a été obtenue dans le cas de la polymérisation thermique initiée par l'azobisisobutyronitrile. Le gel polymérisé conserve la structure initiale, mais les raies de diffraction sont toujours assez floues. Comme dans le cas précédent le gel polymérisé conserve intacte sa structure à température ordinaire.

Le 10-styrylundécanoate de potassium a été polymérisé à température ordinaire en présence de divinylbenzène. Deux cas différents sont à distinguer ici: (*a*) si la polymérisation affecte un gel de structure lisse ($c = 0{,}70$ à $c = 0{,}80$), elle laisse intact le système mésomorphe; (*b*) si elle affecte au contraire la structure médiane ($c < 0{,}60$), l'organisation de celle-ci se trouve totalement détruite au cours de la polymérisation.

c. Etude de la Stabilité des Polymères Organisés. Il nous a paru intéressant d'examiner la structure du gel polymérisé en présence de quantités d'eau différentes de la teneur en eau propre du gel initial. Tous les polymères réticulés ont donc été séchés, puis remis en présence de quantités croissantes d'eau. Macroscopiquement on observe dans tous les cas un fort gonflement. Mais du point de vue structural il existe une différence importante entre les polysavons de type lisse et ceux du type médian: alors que les polymères préparés en phase lisse ne forment avec l'eau que des phases lisses ($c = 1{,}00$ à $c = 0{,}70$), les polymères préparés

dans la phase médiane donnent naissance à une phase médiane quand la concentration est comprise entre 0,50 et 0,70 et à une phase lisse quand c est supérieur à 0,70. Les paramètres structuraux relatifs à ces trois phases sont indiqués sur les Figures 9 et 10. Dans les deux types de

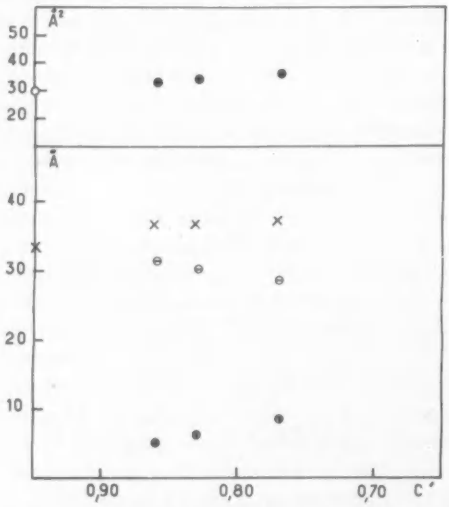

Fig. 9. Variation des dimensions des éléments de structure, en fonction de la concentration du système polysavon–eau, dans le cas d'un polysavon préparé en phase mésomorphe lisse (symboles cf. Fig. 7). Poly 11-styrylundécanoate de Na.

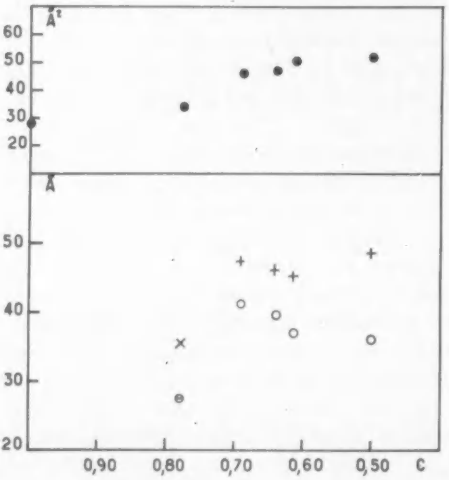

Fig. 10. Variation des dimensions des éléments de structure, en fonction de la concentration, du système polysavon–eau, dans le cas d'un polysavon préparé en phase mésomorphe méd ane (symboles cf. Fig. 7). Poly 11-styrylundécanoate de Na.

polysavon les concentrations qui marquent la limite des possibilités d'absorption d'eau coïncident précisément avec celles des gels initiaux.

Ces observations semblent pouvoir s'expliquer par la présence de liaisons chimiques entre différents éléments de l'édifice mésomorphe. Ces liaisons empêchent de les éloigner les uns des autres à des distances supérieures à celles observées dans le gel initial avant la polymérisation.

2. Polymérisation de Savons Vinyliques Purs

Le 11-styrylundécanoate de sodium présente à température élevée une phase à rubans. Nous avons fait divers essais de polymérisation et de réticulation de ce monomère à différentes températures (170–240°C) et nous avons constaté que la polymérisation n'affecte que fort peu la structure du gel initial. Les groupes polaires restent localisés sur les rubans initiaux; les chaînes remplissent l'espace entre les rubans, mais les rubans se localisent non plus suivant le réseau rectangulaire bidimensionnel initial, mais suivant le réseau hexagonal de paramètre le plus proche.

Les 10-styrylundécanoates de sodium et de potassium ne présentent à température ordinaire que des phases mésomorphes mal définies. Aussi avons-nous renoncé à étudier la polymérisation de ces monomères à l'état pur ou en mélanges hydrocarbonés.

Le 10-styrylundécanoate de calcium présente à température ordinaire une phase à cylindres bien définie. L'addition de quelques pourcents de divinylbenzène améliore encore la finesse des raies de diffraction.

Nous avons fait polymériser des mélanges de savon de calcium avec 5–20% de divinylbenzène par irradiation ultra-violette prolongée en présence de peroxyde de ditertiobutyle comme photosensibilisateur. Ici encore la polymérisation laisse intact le système liquide cristallin et n'entraîne aucune variation des paramètres structuraux.

CONCLUSION

On peut résumer en quelques lignes l'ensemble des résultats expérimentaux.

(*1*) En phase ternaire (eau–savon–monomère) il y a toujours démixtion du polymère formé, quelles que soient la polarité du monomère, la nature de l'initiateur et l'affinité du polymère pour le milieu paraffinique dans lequel il est censé se former.

(*2*) Dans le cas des systèmes binaires en revanche, il nous a été possible, dans certains cas, de "figer" la structure mésomorphe par polymérisation du monomère inclus. Cette réaction se déroule donc effectivement dans le milieu ordonné et le gel "rigidifié" garde les propriétés d'anisotropie et d'organisation du mélange initial. Mais l'extraction du savon conduit à un effondrement de la structure.

(*3*) Seule la polymérisation de savons vinyliques en phase mésomorphe conduit à d'authentiques polymères organisés. Le savon joue ici à la fois le rôle de l'amphiphile, générateur de la phase mésomorphe, et celui du

monomère qui en fige la structure. Toutes les propriétés cristallographiques et optiques du gel initial sont conservées dans le milieu polymérisé.

Ces résultats suggèrent quelques remarques relatives aux paramètres qui conditionnent la réussite, ou l'échec des expériences.

L'étude structurale des phases mésomorphes des colloïdes d'association n'est possible que lorsque les systèmes se trouvent à l'équilibre thermodynamique. Cette condition doit donc être respectée par le système initial savon–(eau)–monomère; il serait évidemment souhaitable qu'elle le soit également par le système final formé de polymère. Toutefois ce cas idéal est rarement rencontré dans la pratique. En général, lorsqu'on a séparé le polymère du savon, il est difficile de reconstituer par mélange un système mésomorphe.

Il est nécessaire dans ces conditions que la polymérisation ait lieu au sein des édifices liquide–cristallins, et que les molécules de monomère ne quittent pas la phase mésomorphe pour se polymériser en une phase séparée. Par ailleurs, même lorsque la polymérisation se produit en phase mésomorphe, il est nécessaire que la vitesse de diffusion des différents éléments (eau, savon, polymère) soit lente devant la vitesse de polymérisation, afin qu'une configuration métastable puisse être figée.

Nous tenons à remercier M. Sadron, qui a bien voulu suivre notre travail avec intérêt, en nous aidant bien souvent de ses conseils.

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Résumé

Des monomères engagés dans des édifices mésomorphes, obtenus en présence de détergents, ont été polymérisés, avec l'espoir d'obtenir des polymères de structures particulières. Les résultats de notre étude peuvent être classés en trois groupes. (*1*) Lorsque le gel est constitué d'un mélange ternaire savon–eau–monomère, la polymérisation s'accompagne de l'expulsion du polymère de la phase mésomorphe. Le polymère ainsi formé ne présente aucune propriété particulière qui pourrait rappeler l'organisation initiale. (*2*) Lorsque le mélange liquide cristallin est formé de savon et de monomère, il est possible, dans certains cas, de provoquer la polymérisation du monomère inclus en conservant la structure initiale du système. Toutefois le polymère, après séparation du savon, ne semble pas présenter de propriétés rappelant celles du gel initial. (*3*) En utilisant des savons vinyliques, on dispose de molécules, qui jouent simultanément le rôle de l'amphiphile promoteur de la phase liquide cristalline et celui de monomère. Des expériences ont été effectuées aussi bien en présence d'eau qu'en système mésomorphe anhydre. La polymérisation permet d'obtenir, dans la plupart des cas, des polymères "organisés" dont la structure est celle du gel initial. Les diagrammes de diffraction des rayons X sont inchangés après polymérisation des échantillons, de même que l'anisotropie optique. Des expériences de gonflement par l'eau ont été effectuées dans le but d'examiner la stabilité des structures des polysavons organisés.

Synopsis

Polymerizations have been carried out in liquid crystalline soap gels in order to attempt to solidify such anisotropic structures. Our experiments led to the following results. (*1*) If the liquid–crystalline gel is a ternary mixture of soap, water and monomer, polymerization always destroys the structure. The polymer is expelled and does not show any peculiar properties which would remind one of the initial organization. (*2*) In the case of binary liquid–crystalline mixtures of soap and monomer, we have found a few cases in which the polymerization of the inserted monomer was possible without a phase separation and collapse of the liquid–crystalline structure. But these media cannot be soaps has been the most successful one. Here the soap is altogether the amphiphile which ensures the formation of liquid–crystalline phases, and the monomer whose polymerization will solidify it. Experiments have been carried out both in binary mixtures of soap and water and in one component systems. Polymerization leads usually to organized polymers, in which the initial gel structure is maintained and even stabilized. X-ray diagrams are unchanged, as is the optical anisotropy. Swelling experiments with water have been carried out in order to demonstrate the stability of the structure of the obtained organized polymers.

Zusammenfassung

Polymerisationsversuche wurden in konzentrierten mesomorphen Seifenlösungen durchgeführt, um dadurch die Struktur dieser Gelen zu erstarren. Unsere Versuche ergaben folgende Ergebnisse. (*1*) Im Falle einer ternären Mischung, Seife–Wasser–Monomer, wird die Struktur infolge der Polymerisationsreaktion immer zerstört. Das Polymer verlässt, während seiner Bildung, die mesomorphe Phase und verzeichnet keine Eigenschaften welche an die ursprüngliche Organisation erinnern. (*2*) Bei binären Seife–Monomer Gelen ist unter bestimmten Bedingungen die Polymerisation des eingeschlossenen Monomers möglich, ohne dass dadurch eine Abscheidung des Gebildeten Polymers oder die Zerstörung der mesomorphen Struktur erfolgt. Es handelt sich in diesem Falle nicht um "organisierte" Polymere, da die Abtrennung der Seife ein Polymer ergibt, welches keine Eigenschaften besitzt, die denen der ursprünglichen Struktur gleichen. (*3*) Der meist erfolgreiche Fall ist jener der Vinylseifen. Die Seife ist hier gleichzeitig das für die Bildung der mesomorphen Phase verantwortliche Amphiphil und das Monomer welches die Struktur durch Polymerisation erstarren lässt. Die

Versuche wurden ebenso in binären Seifen–Wasser Mischungen als auch in wasserfreien Systemen durchgeführt. In den meisten Fällen ergibt die Polymerisation organisierte Polymere, in denen die ursprüngliche Struktur erhalten bleibt. Die Röntgenstrahlendiagramme unserer Proben vor und nach der Polymerisation, sind unverändert, sowie auch die optische Anisotropie. Es wurden Schwellungsversuche mit Wasser durchgeführt um die Stabilität der Struktur der erhaltenen organisierten Polymere zu prüfen.

Discussion

M. Pierrot (*Sté Prögil, Lyon, France*): J'aimerais savoir quels types de styrènes initiateurs sont utilisables pour la polymérisation en milieu mesomorphe en phase aqueuse et quelle est dans ce cas la technique d'introduction de l'initiateur?

J. Herz: Nous avons utilisé des promoteurs solubles aussi bien en phase aqueuse qu'en phase hydrocarbonée.

Dans le premeer cas le promoteur est dissous dans l'eau avant préparation du mélange.

Dans le deuxième cas/: (*1*) si l'on polymèrese un savon vinylique, le promoteur est introduit dans le savon avant préparation du mélange; (*2*) si l'on polymérise un monomère inclus dans une structure mésomorphe, le promoteur est dissous préalablement dans lè monomère.

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Organized Polymerization. I. Olefins on a Clay Surface

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In the course of an experimental program on the polymerization of monomers constrained[1–4] by being intercalated in montmorillonite,[5] it was found that butadiene polymerizes spontaneously at room temperature and atmospheric pressure on the external surface of neutral montmorillonite without additional catalysis. This report treats the polymerization of butadiene, *cis*-butene-2, and *trans*-butene-2 on the external surface of neutral and acidic montmorillonite. This type of polymerization for butadiene has been loosely described in a patent,[6] but not studied in any detail. This is believed to be the first report of the homopolymerization of either form of butene-2.

A. THE CLAY

Montmorillonite is a layered mineral made up of condensed tripartite units consisting of two tetrahedral silica sheets surrounding a central octahedral alumina sheet. Substitution in the alumina layer by magnesium and iron can be extensive. When dry, the *c* spacing distance between units in the natural sodium form is 9.6 A. Upon intercalation by one or more layers of foreign molecules, the *c* spacing expands.[7] Although it has been reported that intercalated complexes of benzene, naphthalene, and decalin have been formed with the ammonium salt of montmorillonite,[8] this has been disputed.[9] For organic salts, intercalation of symmetrical hydrocarbons would appear possible,[10] in contrast with Blumstein's criterion of dipole moment.[5] In any case, our work with sodium montmorillonite showed no intercalation of butadiene by the criteria of apparent surface area and *c* spacing (x-ray analysis by Dr. R. M. Valletta).

Our montmorillonite is natural Wyoming bentonite (Aquagel, Baroid Division, National Lead Co., Houston, Texas) in its original form dried at 100°C. This has an external surface area of about 85 $m.^2/g.$[11] The external surface area can be increased to 300 $m.^2/g.$ when activated with boiling acid. If the internal area achievable by intercalation were involved, the figure would be 800 $m.^2/g.$[5,7] The ion-exchange capacity varies with cation, but is about 1 meq./g.[7,12,13] The surface was dried by continual storage at 90–100°C. and heating to 150°C. under a vacuum of 10^{-3}–10^{-4} Torr for 18 hr. prior to each experiment.

B. EXPERIMENTAL PROCEDURES AND RESULTS

Three types of polymerizations were performed: (*a*) solid–gas experiments at reduced pressure in a gravimetric microbalance on 1-g. samples at various temperatures, (*b*) solid–gas experiments at room temperature in one-liter autoclave at equilibrium pressure (butadiene, 2.6 atm. *cis*-butene-2, 1.95 atm.); (*c*) solid–liquid experiments at −78° or 0°C. for pure monomer, or as in (*b*), for monomer dissolved in solvent at room temperature.

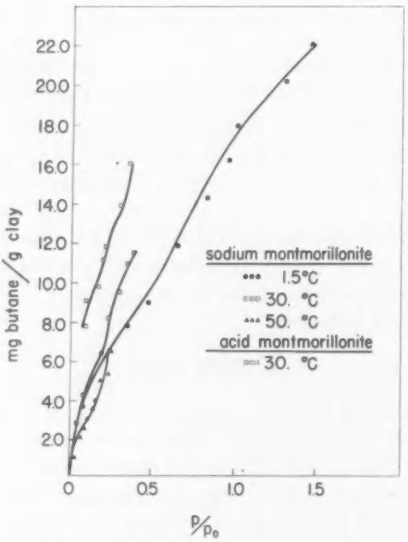


Fig. 1. Adsorption of butane on montmorillonite.

Most of the data presented here were obtained from reading a thermostated, evacuated, quartz-helix microbalance. The helix is displaced 20 cm. in reading 2.0 g., while the cathetometer employed can be read to ±0.02 mm. or ±0.2 mg.

In each case the sample, weighing approximately 1 g., is dried by heating and evacuation because the olefin cannot be adsorbed in the presence of surface water. Then, after equilibration to the temperature of choice, the olefin is admitted to the microbalance, normally at one-tenth of the equilibrium pressure for that temperature ($p/p_0 = 0.1$). The amount of adsorbed monomer is noted on the microbalance. After a given amount of polymerization time, the vacuum (10^{-3}–10^{-4} Torr) is applied to remove monomer. Constant weight is achieved within 10 min., but has been checked many times for 18 hr. The increase in weight in vacuum is attributed to polyolefin.

Since butadiene polymerizes on the surface of the neutral sodium form of montmorillonite, a true adsorption isotherm cannot be measured for it. Some data for the adsorption of *n*-butane on this substrate are shown in Figure 1, as well as one curve for the acid form. From Figure 1, we see that the energy of activation for the adsorption of butane on sodium montmorillonite is low, and that there is no layering at these pressures. The molecular cross-sectional area of butane varies in the range of 32–45 A.^{2}, depending on author and method.[14] Assuming 40 A.^{2} for the area of butane and 80 m.^{2}/g. for this clay, the hypothetical monolayer for butane can be computed as 19 mg./g. clay.

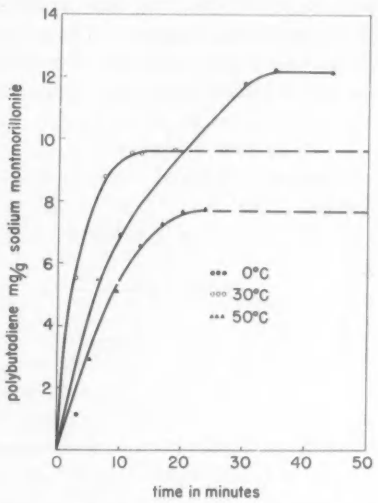


Fig. 2. Polymerization of butadiene on sodium montmorillonite.

In Figure 2 the extent of polymerization at various temperatures is shown with time, all runs at a constant pressure $p/p_0 = 0.1$. It is seen that the amount of polymer approaches a definite limit and that this limit decreases for rising temperature in the range 0–50°C. This is not to say that no more monomer is adsorbed with increasing time at constant pressure, but only that the polymerization stops. There is some evidence that the amount of adsorbed monomer is constant during the coating process, but superimposed, of course, on a gradually increasing amount of polymer. If the calculation of the hypothetical monolayer for butane has any validity for butadiene, the coating of polymer is not multilayered. For the weight of monomer adsorbed the polymerization is several orders of magnitude faster than the purely thermal rate.[15]

More striking is the polymerization of the hindered olefin *cis*-butene-2 under these mild conditions. It is generally considered that symmetrical,

disubstituted, ethylenically unsaturated compounds of this type can participate in copolymerization, but are difficult to homopolymerize. True, the homopolymerization of liquid maleic anhydride has been reported recently under forcing conditions:[16] radiation with gamma rays for 100 hr., 5% benzoyl peroxide for 48 hr., or catalyzed ultraviolet irradiation for 27 days. Butene-2 copolymers with ethylene have been made by the Ziegler-Natta type of catalyst, but it was reported[17] that no butene-2 homopolymers were made.

The rate of polymerization of *cis*-butene-2 adsorbed on neutral sodium montmorillonite at 0 and 30°C. is shown in Figure 3 at $p/p_0 = 0.1$. The effects of temperature noted with butadiene did not hold for *cis*-butene-2. That is, the adsorption was not higher at 0 than at 30°C., and the amount of polymer formed also was about the same. The coverage of monomer is less than for butadiene. Even less coverage is obtained by using *trans*-butene-2, which does not polymerize on sodium montmorillonite by this procedure.

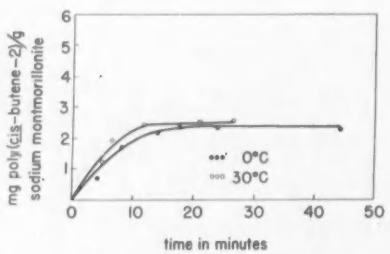


Fig. 3. Polymerization of *cis*-butene-2 on sodium montmorillonite.

For a 1-g. sample of sodium montmorillonite at 30°C. the three olefins, each one at its $p/p_0 = 0.1$ pressure, are adsorbed in the amounts: butadiene, 10.2 mg./g.; *cis*-butene-2, 7.5 mg./g.; *trans*-butene-2, 5.7 mg./g. Furthermore, this heterogeneity of the surface is reinforced by the fact that once the typical amount of polybutadiene has been formed on a given sample, then *cis*-butene-2 can be introduced and polymerized in approximately its normal amount in addition.

Although each isomer is certified by the producer (Matheson Co., East Rutherford, New Jersey) as being greater than 99 mole-% pure, there is some *cis*-impurity in the *trans* and some *trans*-impurity in the *cis*. Initial experiments showed so little polymer from the *trans*-butene-2, that it was hypothesized that this trace amount was from polymerization of its *cis*-impurity. Therefore, a reservoir was set up for pretreatment of *trans*-butene-2 in the same one-liter autoclave used for treatment of larger amounts of clay (procedure *b*). By storing one liter of *trans*-butene-2 for several days at cylinder pressure (1650 cm.) over 200 g. of the activated sodium montmorillonite, all the *cis*-butene-2 was removed as polymer on

the clay in the reservoir. The purified product from this pretreatment did not form in 18 hr. of treatment at $p/p_0 = 0.1$ even the trace amounts of polymer observed in the earlier experiments. Hence, the statement is made that *cis*-butene-2, but not *trans*-butene-2 polymerizes when adsorbed at ambient temperature on neutral sodium montmorillonite.

As shown in Figure 1, and as studied in detail by Dietz et al.,[11] the surface area of natural montmorillonite is increased by treatment with strong acid to make the hydronium salt. In our case, the capacity to adsorb butane is doubled. At this writing the polymerization of the three olefins on acid montmorillonite has not been studied in detail; nevertheless, the following can be said regarding the preliminary experiments: (*1*) all three monomers polymerize; (*2*) the polymerization is faster than for the sodium form; (*3*) the polymerization is limited as in the case of the sodium salt.

In an effort to increase the extent of polymerization beyond a two-dimensional layer, the sodium montmorillonite was exposed to liquid butadiene (procedure *c*). This reaction did not propagate in the liquid. The polymerization of *cis*-butene-2 was carried out at room temperature at equilibrium pressure (1.95 atm.) in a stirred autoclave containing a suspension of sodium montmorillonite in benzene. Again, only the characteristic coating of polymer formed on the clay.

C. DISCUSSION

Effect on the Clay

Although the surface polymerization of a hydrocarbon on the montmorillonite represents an increase in weight of only 1%, the effect on the clay is profound. This partial surface coating is sufficient to render the clay hydrophobic, and a pink-brown color is readily apparent.

Possible Impurities

There are several major difficulties in analyzing this reaction. Firstly, there is the apparent heterogeneity of the surface. This may be due to minute amounts of water or oxygen. Without the gross removal of water from the surface no polymerization takes place. However, variations in degree of dehydration may be the explanation for the uneven uptake of monomer. The loss in weight on vacuum drying is equivalent to heating the clay to 550°C., where the composition is stable to 1000°C. In all cases the amount of polymer is limited against time in a parabolic manner as described above, but the adsorption of monomer by the product is not reproducible varying from zero to amounts comparable to the initial uptake. Even more difficult is control of the amount of air. At best our combination of mechanical and diffusion pump produces a vacuum of 10^{-5} Torr. Of course, this is not enough to furnish a truly clean surface. In one trial the polymerization of butadiene on sodium montmorillonite was carried out in the presence of 0.25 atm. of dry air. Although air competed for the

surface with the monomer (as measured gravimetrically) and the yield was diminished by one-half, there was no induction period. Thus, varying amounts of air on the surface could be responsible for varying yields, complicating the kinetic picture.

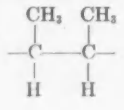
Extraction

The polymerization presumably takes place in a two-dimensional, mobile layer on the surface. Although the energy of adsorption of the monomer is low (see Fig. 1), the polymer is so tightly adsorbed to the surface that only a low molecular weight fraction can be extracted by boiling aromatic solvents. For butadiene this would not be surprising, since at high conversions crosslinking can occur.[18] In practice, however, it was found that more polybutadiene could be extracted than polybutene-2, even though extraction of the latter was carried out with solvents boiling as high as 281°C. (α-bromonaphthalene). It is possible that the polybutadiene is strongly bonded to the clay, particularly through adsorbed oxygen. Yet, a determination of iodine number (analyses carried out by T. Fazio and S. Jaffe) consistently showed one-half the unsaturation still available on the bound polymer by the ordinary procedure intended for low molecular weight organic molecules in solution. More forcing procedures for determining iodine number carbonized the polymer. About 10–15% of the butadiene made on sodium montmorillonite could be extracted by benzene. This showed a reduced viscosity of 0.2 at 0.2% solution. Of the polybutadiene made on acid montmorillonite, 40% could be extracted; this showed a reduced viscosity of 0.16 for the 1% solution. From sodium montmorillonite the first extraction gave a polymer substantially pure *cis*-1,4. The second extraction gave a polymer containing approximately equal amounts of *cis*-1,4 and *trans*-1,4 with minor amount of the 1,2 form. It should be emphasized, however, that in all cases most of the polymers could not be extracted.

In all cases only trace amounts of the poly-*cis*-butene-2 could be extracted. Molecular weights by depression of the melting point of camphor (Schwarzkopf Laboratory, Woodside, N. Y.) gave an average value of 482 for the oil fraction and 468 for the wax fraction corresponding roughly on average to the monomer.

Infrared Spectra

The infrared spectra of both these fractions of the polymer of *cis*-butene-2 are shown in Figure 4 along with the spectrum of the polymer of diazoethane published by Nasini et al.[19] Our polymer of *cis*-butene-2 should be a chain of the recurring unit:



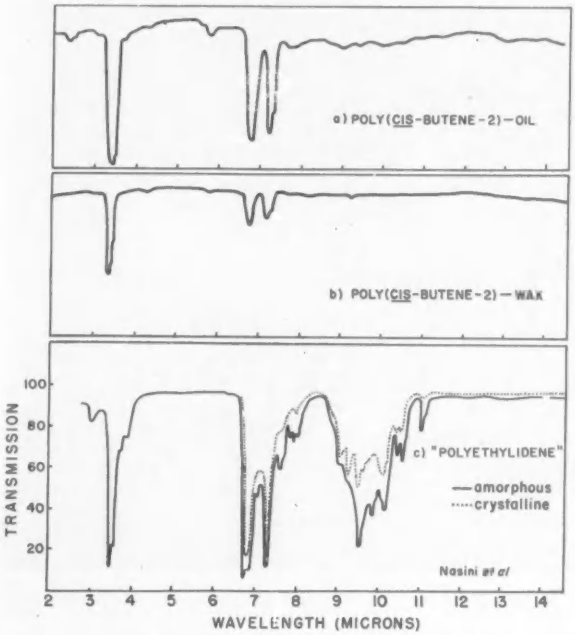
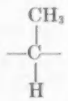


Fig. 4. Infrared absorption spectra of polybutene-2 and polyethylidene.

while polyethylidene would be a chain of the recurring unit:



Configurational aspects aside, the infrared absorption spectra should be the same. The "polyethylidene" of Nasini is, in fact, highly unsaturated, as shown by the strong absorption bands in the region of 9–11.5μ. This internal and vinyl unsaturation is discussed by Nasini.[19] The remainder of Nasini's spectrum corroborates the structure of poly-*cis*-butene-2. At this writing it is not known if our waxy and oily fractions of the same molecular weight have different stereochemical configurations.

Type of Reaction

One hesitates at this point to classify the polymerization of olefins on montmorillonite as either free radical or ionic. The preponderance of evidence, however, favors the former. A potential argument for a free radical mechanism is the finding of a high concentration of organic free radicals in the clay.[20] In Figure 5 characteristic electron spin resonance differential spectra for natural Wyoming bentonite and for diphenylpic-

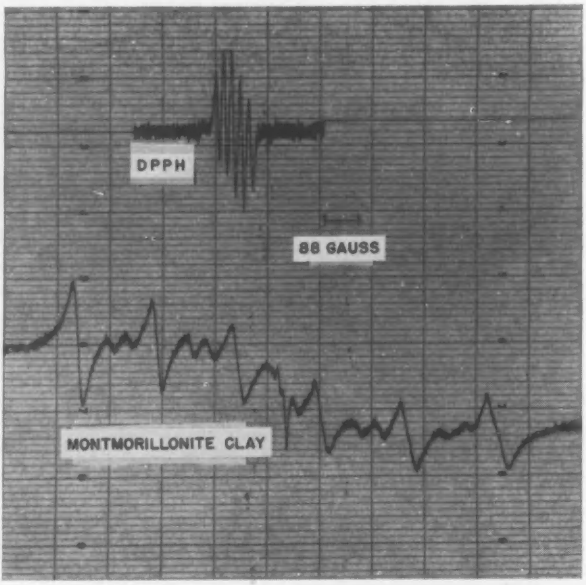


Fig. 5. Electron paramagnetic resonance spectrum of natural montmorillonite.

rylhydrazyl (DPPH) at the same machine settings are shown The signal for an anisotropic organic free radical is seen at the center of the clay spectrum superimposed on the 18-peak spectrum of a manganese impurity. This spectrum persists after both the limit surface polymerization of olefins and also after the different polymerization of liquid styrene. When liquid styrene is the monomer, the reaction is propagated into the solution yielding copious amounts of polystyrene. This solubilization of the polymeric product in the case of styrene cleans the surface of the clay leaving it hydrophilic, rather than hydrophobic after the polymerization of olefins described in this communication. The characteristic central dip is eliminated after heating in air for 20 hr. at 250°C., or after heating for 2 hr. in air at 480°C. or after heating for 2 hr. in air at 480°C.

The fact that the free radical in the clay is so stable and that the olefin polymerization can be carried out in the presence of massive amounts of oxygen (*vide supra*) give pause to assigning a free radical mechanism. It is possible that copolymerization by a free radical mechanism with trace amounts of oxygen takes place.[18,21] No evidence for this was observed in the infrared spectra of polybutadiene or poly-*cis*-butene-2, however.

With regard to mechanism it may be mentioned that an attempt to study the polymerization by gamma rays of butadiene adsorbed on various types of carbon black has been reported.[22] The samples were prepared at one laboratory, irradiated with 10–25 Mrep at Brookhaven, and analyzed several weeks later. The results were unreproducible, and the authors

state that the polymerization may be unrelated to the radiation. The pK of these carbon blacks is unreported. One might take this evidence as more related to free radical polymerization than ionic.

As for the energy of activation of our reaction, the data shown in Figure 2 indicate no effect of temperature on the initial rate of polymerization. Even when the formation of free radicals is eliminated from a kinetic study by the presence of long-lived free radicals already formed, as in radiation grafting, there is normally an energy of activation for rate of polymerization of 4.5–4.8 kcal./mole.[23] In our case, the lack of increase in rate with higher temperature may be counterbalanced by decreasing amount of adsorbed monomer.

Acid Clay

The acid form of montmorillonite is, of course, a strong Lewis acid.[13] That more polymer can be extracted from the acid montmorillonite may be an indication of a different mechanism, but this has not yet been established. It may also be questioned whether there is enough water on the external surface of the acid montmorillonite under our conditions to serve as a cocatalyst.

In the case of acid montmorillonite to specify whether the polymerization is free radical or ionic may be an oversimplification in view of recent evidence that aromatic organic molecules adsorbed on acidic sites form radical-ions.[24–26] The various authors cited do not agree on the role of oxygen. It is found necessary by Fogo[24] and deliterious for radical formation by Rooney and Pink.[26] The latter distinguish for silica–alumina between Lewis acid sites where the radical-ions are formed and exchangeable Brønsted sites where "polymerization" takes place. The nature of this polymerization was unreported; it may be the formation of dimer and trimer termed polymerization by the petroleum industry.

D. CONCLUSIONS

1. A spontaneous polymerization of butadiene and *cis*-butene-2 takes place on the surface of neutral sodium montmorillonite (Wyoming bentonite) under mild conditions.

2. On the acid form of this substrate the *trans*-butene-2 isomer is also polymerized.

3. The polymerization of these monomers is limited to a tightly adsorbed layer, presumably two-dimensional.

4. The polymerization may be associated with organic free radicals observed by EPR in the natural clay, yet the mechanism is not clear.

It is a pleasure to acknowledge the experimental assistance of Messrs. Joseph Bobko and Mario Ferro.

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Synopsis

The spontaneous polymerization of monolayers of butadiene and butene-2 adsorbed on the sodium form of montmorillonite (Wyoming bentonite) has been studied from −78 to 60°C. For this particular form of montmorillonite with these monomers evidence is shown that there is no intercalation and that only the external surface is involved. The surface appears to be heterogeneous for these monomers in that the amount of coverage and hence the amount of polymer increases in the sequence *trans*-butene-2, *cis*-butene-2, butadiene. It is considered noteworthy that a homopolymer of such hindered, symmetrical monomers such as the butene-2's forms under such mild conditions. These monomers can only be copolymerized with ethylene up to 50%, but not homopolymerized, by the Ziegler-Natta type of initiation. The adsorption of these olefins is compared to that of butane over this temperature range. The rates of polymerization are shown for 0, 30, and 50°C. as determined on a microbalance. The mechanism of the initiation is discussed, and the apparent energies of activation are shown. A comparison between the polymerization on the neutral substrate and the corresponding acid form of the clay is made.

Résumé

On a étudié la polymérisation spontanée de couches monomoléculaires de butadiène et de butène-2, absorbés sur la forme sodée de la montmorillonite (bentonite du Wyoming) dans les domaines de température de −78° à 60°C. On démontre que pour cette forme particulière de montmorillonite avec de tels monomères, il n'y a pas d'intercalation et que seule la surface externe est employée. La surface apparaît hétérogène pour ces monomères de sorte que la quantité de recouvrement et de là la quantité de polymère augmente dans l'ordre *trans*-butène-2, *cis*-butène-2, butadiène. On considère notamment qu'un homopolymère provenant de monomères symétriques tels que le butène-2 se forme dans de telles conditions modérées. Ces monomères ne peuvent être copolymérisés qu'avec l'éthylène jusqu'à 50%, mais s'ils ne peuvent être homopolymérisés par initiation du type Ziegler-Natta. L'adsorption de ces oléfines est comparée à celle du butane dans ces domaines de température. Les vitesses de polymérisation sont déterminées à 0°, 30° et à 50°C par microbalance. On discute le mécanisme d'initiation et on calcule les énergies d'activation apparentes. On fait la comparaison entre la polymérisation sur un substrat neutre et la forme acide correspondante de l'argile.

Zusammenfassung

Die spontane Polymerisation monomolekularer, auf Natrium-Montmorillonit (Wyoming-Bentonit) adsorbierter Butadien- und Buten-2-schichten wurde im Bereich von −78° bis 60°C untersucht. Bei dieser speziellen Montmorillonitform tritt keine Aufnahme der untersuchten Monomeren in das Gitter, sondern nur Adsorption an der äusseren Oberfläche ein. Die Oberfläche scheint für diese Monomeren insofern verschiedenartig zu sein, als der Bedeckungsgrad und damit die Polymermenge in der Reihenfolge *trans*-Buten-2, *cis*-Buten-2, Butadien zunimmt. Es erscheint bemerkenswert, dass sich unter so milden Bedingunge ein Homopolymeres aus gehinderten, symmetrischen Monomeren, wie Buten-2, bildet. Mit Ziegler-Natta-Katalysatoren lassen sich diese Monomeren nur bis zu einem Gehalt von 50% mit Äthylen copolymerisieren. Die Adsorption der Olefine wird mit der von Butan im gleichen Temperaturbereich verglichen. Polymerisationsgeschwindigkeiten wurden bei 0°, 25°, 30°, und 50°C an der Mikrowaage bestimmt. Der Startmechanismus wird diskutiert und die scheinbaren Aktivierungsenergien berechnet. Ein Vergleich zwischen der Polymerisation an der neutralen und der entsprechenden sauren Form des Katalysators wird durchgeführt.

ELECTRONIC PROPERTIES OF NATURAL AND SYNTHETIC POLYMERS

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1305–1313

Synthesis and Study of the Photoelectric Properties of Polyazines and Schiff Polybases

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Recently polymers with a system of conjugate bonds in their main chain have been drawing the attention of researchers more and more. The methods of obtaining such polymers and studying their properties are dealt with in a number of papers.[1,2] Polymers with a system of conjugated —C=C— and —C=N— bonds have been shown to possess interesting electrophysical, particularly, semiconductor properties.

Of interest among polymers containing conjugate bonds in their fundamental polymeric chains are polyazines and poly-Schiff bases. The presence in the compounds, $(=CX—R—CX=N—N=)_n$, where X is H, CH_3, or C_6H_5, and $(=CX—R—CX=NC_6H_4—N=)_n$ where X is H, CH_3, or C_6H_5, of nitrogen heteroatoms with free electron pairs create favorable conditions for maximal sharing of π-electrons of the conjugate bonds. In connection with this we undertook an investigation of the synthesis of polyazines and poly-Schiff bases. The polyazines were obtained by the reaction of polycondensation of hydrazine with a number of diketones. The poly-Schiff bases were produced by polycondensation of *p*-phenylenediamine with various dicarbonyl compounds. To study the effect of the degree of conjugation in the macromolecule on the electric properties of the polymers, substances were synthesized with methylene groups, as well as oxygen and sulfur atoms in their macromolecules.

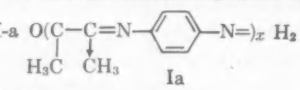
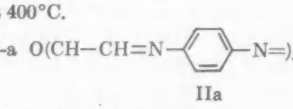
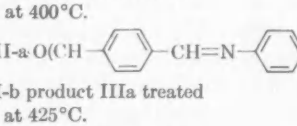
The initial diketones and dialdehydes used were glyoxal, diacetyl, benzyl, 4,4′-diacetyldiphenyl oxide, 4,4′-diacetyldiphenyl sulfide, 4,4′-diacetyldiphenylmethane, 4,4′-diacetyldiphenyl ether of ethylene glycol, and terephthalic dialdehyde The resulting polymers are solid, colored substances. Darker shades are characteristic of polymers with a continuous conjugation chain. These substances dissolve very sparingly in common organic solvents, somewhat better in tetrachloroethane and dimethylformamide, and readily in phenol and in sulfuric and formic acids. Most of the polyazines possess a crystalline structure. The infrared spectra of the above-named polymers reveal the presence of an intense absorption band at 1670 cm.$^{-1}$ characteristic of the valence vibrations of the C=O bond, and 1600 cm.$^{-1}$ bands, which are indicative of the presence of C=N bonds.

Unlike the polyazines, poly-Schiff bases possess considerable heat resist-

ance. Thus, in the case of the product of polycondensation of terephthalic dialdehyde and *p*-phenylenediamine the main process, which continues up to 425°C., is further polycondensation, this being evidenced by the decrease in intensity of the band of the carbonyl endgroup in the infrared spectrum. Apparently, the drop in solubility of the polymer is a result of molecular weight increase. In the 425–500°C. temperature range the predominant processes probably involve intramolecular regrouping, as is evidenced both by the absence of any weight loss, and the decrease in intensity of the 1,4-benzene substitution band in the infrared spectrum. Drastic destruction connected with the generation of perceptible quantities of liquid and gaseous pyrolysis products sets in at 570°C. and over. It is characteristic that though there is no change in weight of the polymer in the 425–500°C. interval, the electrical conductivity is observed to increase by fair orders. Possibly, the increase in conductivity is due to the formation of condensed and three-dimensional aromatic structures.

The process of thermal conversion of poly-Schiff bases obtained from aliphatic carbonyl compounds is substantially different. Already in the early stages of thermal conversion the process of further polycondensation is accompanied by drastic degradation, manifested in a considerable weight loss when heated to 250°C. Such great destruction is connected with the presence of aliphatic bonds in the chains. The data in Table I give an idea of the nature of change in elementary composition during heat treatment.

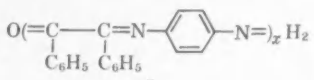
TABLE I

Initial polymers and their heat treatment products	C, %	H, %	N	C—G, %	Weight loss, %
I-a  Ia	68.68	6.38	12.18	10.8	0
I-b Product Ia Treated at 250°C.	68.68	5.82	13.45	11.8	12.80
I-c product Ia treated at 400°C.	74.08	4.83	13.53	15.3	35.00
II-a  IIa	62.40	5.25	13.06	11.9	0
II-b product IIa treated at 250°C.	64.48	4.54	15.11	14.20	13.20
II-c product IIa treated at 400°C.	70.90	4.46	15.12	15.9	36.00
III-a 	78.88	5.08	12.90	15.5	0
II-b product IIIa treated at 425°C.	82.31	4.34	11.39	18.9	10.30
III-c product IIIa treated at 500–570°C.	78.60	3.38	10.84	23.2	26.0

An exponential conductivity vs. temperature dependence is characteristic of these polymers. Data on the electric properties of some of the polyazines and poly-Schiff bases synthesized by us are listed in Table II. At room temperature the specific conductance of polymers with conjugate double bonds is in the range 10^{-11}–10^{-14} ohm^{-1} cm.$^{-1}$. Introduction of a methylene group between the phenyl nuclei does not, evidently, result in any perceptible change in the polymer electrical properties. This is in agreement with recent data[5] which indicate that the decrease in the degree of conjugation may be compensated by an increase in crystallinity. Introduction of oxygen and sulfur atoms between the phenyl nuclei raises the polymer conductivity slightly. When the phenyl nuclei are separated by two oxygen atoms and two methylene groups the polymer conductivity drops sharply despite its crystallinity.

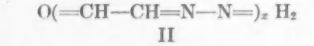
As is known, organic dyes containing systems of conjugate bonds and heteroatoms in their conjugation chains, possess photoelectric sensitivity in the region of their absorption bands, which are situated in the visible part of the spectrum. The polymers that we synthesized are also colored. Either their absorption bands are located entirely in the visible region of the spectrum or this region contains a long-wave band drop with their maximum in the near ultraviolet. This determines the expediency of investigating the photoelectric sensitivity of such polymers in the visible and ultraviolet regions of the spectrum.

The compounds selected for the photoconductivity investigation were: the product of polycondensation of benzyl with *p*-phenylenediamine



I

a representative of the poly-Schiff base group, and the product of polycondensation of hydrazine with glyoxal



II

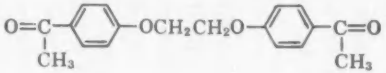
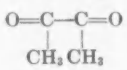
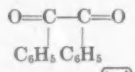
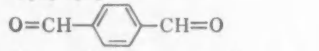
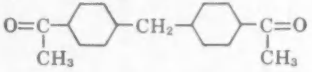
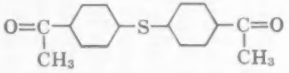
a representative of the group of polyazines. The absorption spectra of the solid layers of these compounds are shown in Figure 1.

The photoconductivity of the polymers was studied with thin films obtained from a solution of the substance in dimethylformamide by evaporating the solvent. The films were prepared directly on flat quartz plates to which platinum electrodes had been applied beforehand. The gap between the electrodes was 1 mm. The films were illuminated by focusing a pencil of white light from a 30-incandescent lamp or by the monochromatic radiation of an SVD-120 mercury lamp in the region of the 4358 A. line. The measuring instrument was an EMU-3 d.c. electrometric amplifier. All investigations were carried out *in vacuo* (10^{-5}–10^{-4} mm. Hg).

In fields not exceeding 1000–1500 v./cm. the photocurrent in polymer I obeys Ohm's law. At larger field intensities, deviations from the ohmic

TABLE II
Properties of Polyazines and Poly-Schiff Bases

No.	Initial dicarbonyl compound	Structural formula	Physical properties: Color	Melting point, °C.	Molecular weight	Crystallinity	Electric properties: Activation energy	Pre-exponential σ^0, ohm^{-1}cm.$^{-1}$	Specific conductance σ_{293}, ohm^{-1}cm^{-1}
			A. Polyazines						
1	Glycosal	O=CH—CH=O	Black	210 (dec.)	—	Amorph.	1.60	9	7×10^{-12}
2	Diacetyl	O=C(CH$_3$)—C(CH$_3$)=O	Yellowish orange	270 (dec.)	—	Cryst.	1.56	2	1×10^{-13}
3	Benzyl	O=C(C$_6$H$_5$)—C(C$_6$H$_5$)=O	Orange	250 (dec.)	4490[a] 5200[b]	Amorph.	2.11	2 $\times 10^4$	1×10^{-14}
4	4,4′-Diacetyldiphenylmethane	O=C(CH$_3$)—C$_6$H$_4$—CH$_2$—C$_6$H$_4$—C(CH$_3$)=O	Light green	237–238	1000[a]	Cryst.	1.88	1 $\times 10^3$	6×10^{-14}
5	4,4′-Diacetyldiphenyl sulphide	O=C(CH$_3$)—C$_6$H$_4$—S—C$_6$H$_4$—C(CH$_3$)=O	Light green	270–271	—	Cryst.	2.46	4 $\times 10^6$	2×10^{-15}
6	4,4′-Diacetyldiphenyloxide	O=C(CH$_3$)—C$_6$H$_4$—O—C$_6$H$_4$—C(CH$_3$)=O	Pale green	280–298 (partial dec.)	1790[c]	Cryst.	2.68	1.7 $\times 10^6$	2×10^{-16}

7	4,4′-Diacetyldiphenyl ether of ethylene glycol		Pale green	255-258	—	Cryst.	2.82	2 × 10^{6}	1 × 10^{-18}
		B. Poly-Schiff bases							
8	Glycosal		Dark brown	Does not melt	—	Amorph.	1.2	0.1	1 × 10^{-11}
9	Diacetyl		Black	Does not melt	—	Amorph.	1.4	0.5	3 × 10^{-13}
10	Benzyl		Dark brown	160-162	900[a]	Cryst.	1.4	5	3 × 10^{-12}
11	Telephthalic dialdehyde		Yellow	340 (dec.)	—	Cryst.	2.08	2.5 × 10^{5}	2 × 10^{-13}
12	4,4′-Diacetyldiphenylmethane		Dark blue	96-100	—	Cryst.	3.6	3.4 × 10^{16}	2.7 × 10^{-16}
13	4,4′-Diacetyldiphenyl sulphide		Brown	98-100	1200[a]	Cryst.	3.5	2.4 × 10^{18}	6 × 10^{-15}

[a] Determined isopiestically.
[b] Determined ebulioscopically.
[c] Determined after rust.

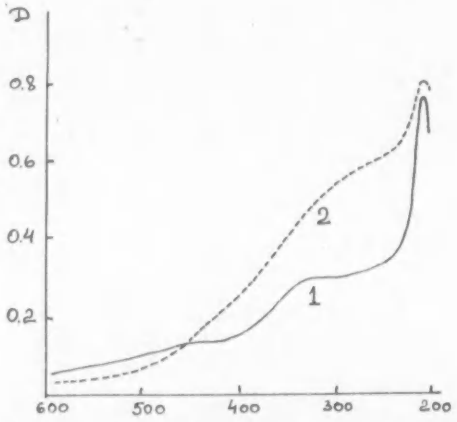


Fig. 1. Absorption spectra of solid polymer layers: (*1*) product of polycondensation of benzyl with *p*-phenylenediamine; (*2*) product of polycondensation of glyoxal with hydrazine.

dependence were observed toward a more rapid current growth. For polymer II Ohm's law was fulfilled over the entire range of field intensities studied (up to 4000 v./cm.). The luxampere dependence of the photocurrent in the polymers is expressed by the relation $i \sim L^n$, the exponent n in our experiments being 0.5–0.6 and 0.8 for polymers I and II, respectively. The magnitude of the photocurrent for the compounds studied depends on the temperature. On heating the polymer film the photocurrent rises according to the exponential law $i \sim e^{-\epsilon\phi/kT}$, where $\epsilon\phi$ equals, respectively, 0.19 (polymer I, temperature range 21–75°C.) and 0.05 e.v. (polymer II, 21–90°C).

Thus, the photoelectric properties of the polymers in question are close to those of earlier studied organic semiconductors. At the same time, they, and especially, polymer I, have characteristic polarization phenomena which manifest themselves in the kinetics of the photocurrent. Nonmonotonous establishment of steady photocurrent on first illumination, and the presence of depolarization currents are characteristic of high-ohmic semiconductors and have been pointed out in papers on photoconductivity of both inorganic[6] and organic[7,8] compounds. At the same time, polarization phenomena have not been observed for a large number of substances, particularly, certain organic dyes which are among the most high-ohmic semiconductor substances in general.[9] In the films of polymer I these phenomena are very distinct. The kinetic curves have the form shown in Figure 2. On first illumination of the film when an external field has been applied to it, the photocurrent reaches a steady value after first passing through a maximum. The current value at the maximum may exceed the steady current value by one order. On repeated illumination the steady photocurrent is established monotonously. The monotonous course of the curve

is retained even when the voltage is temporarily removed in the dark and is then again applied to the sample. When the sample is illuminated without a field, depolarization is observed. The value of the initial throw-off for this current depends on the duration of the dark pause according to a

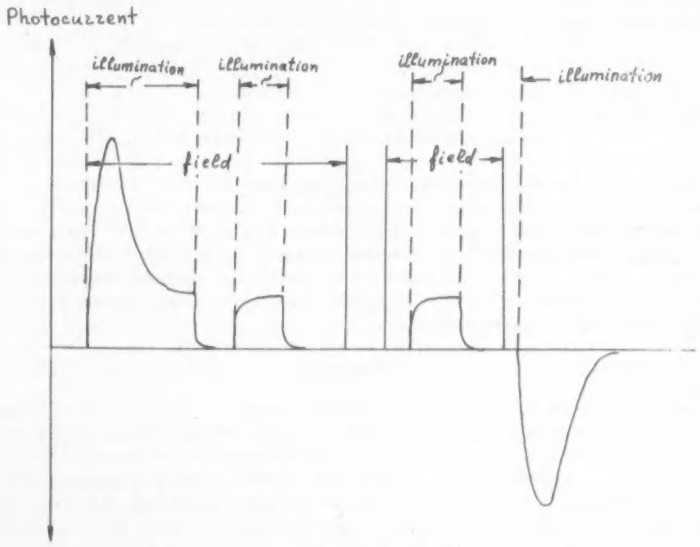


Fig. 2. Kinetics of photoconductivity in polymer I.

hyperbolic law. Therefore, the resorption of the state of polarization in the dark is of a bimolecular nature in this case.

Work in studying the nature of photoconductivity of polymers with a system of conjugate bonds will be the subject of further research.

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Synopsis

The method of linear polycondensation of dicarbonyl compounds with hydrazine or with its salt in organic acids or in a water–alcohol medium with addition of hydroxides of alkali metals as catalysts has been used to produce a number of polyazines. They are colored substances with a relatively low molecular weight and with a very limited solubility in organic solvents. The structure of many polyazines is crystalline. Their resistance depends on temperature and is governed by an exponential law; the energy of activation ranges from 1.56 to 2.82 e.v. and their specific electroconductivity σ_{20} varies from 7.08×10^{-12} to 1.12×10^{-18} ohms^{-1} cm.$^{-1}$. A number of Schiff polybases with a system of conjugated bonds has been synthesized from *p*-phenylenediamines and 2,6-diaminopyridine with carbonyl derivatives: diacetyl, benzyl, glyoxal, terephthalic dialdehyde, maleic dialdehyde, diacetylphenyl oxide, and diacetyldiphenyl sulfide. The color of the resulting polymers was black to grey. The polymers are soluble in dimethylformamide and acetic, formic, and sulfuric acids. The electric properties of Schiff polybases were investigated. The temperature dependence is governed by the equation $\sigma = \sigma_0 e^{-\Delta E/KT}$ and the energy of activation varies from 3.6 to 0.8 e.v.; $\sigma_{20} = 10^{-13}$–10^{-11} ohms^{-1} cm.$^{-1}$. Photoelectric sensitivity has been found in a number of compounds. The voltampere, luxampere, and temperature dependence of photocurrent has been established. The phenomenon of polarization was investigated in the polymer product of the polycondensation of benzyl with *p*-phenylenediamine.

Résumé

On a utilisé pour la formation d'un certain nombre de polyazines la méthode de polycondensation linéaire des dérivés dicarbonyliques avec l'hydrazine ou ses sels en milieu acide organique ou en milieu eau-alcool en présence d'hydroxydes de métaux alcalins comme catalyseurs. Ce sont des corps colorés, de poids moléculaire relativement bas et d'une solubilité limitée dans les solvants organiques. La structure de beaucoup de polyazines est cristalline. Leur résistance dépend de la température et suit une loi exponentielle. L'énergie d'activation couvre un domaine de 1.56 à 2.82 ev et leur électroconductivité spécifique σ_{20} varie de 7.08×10^{-12} à 1.12×10^{-18} ohms^{-1} cm^{-1}. On a synthétisé un certain nombre de polybases de Schiff, ayant un système de liaisons conjuguées, à partir de *para*-phénylènediamine et de 2.6-diaminopyridine d'une part et de dérivés carbonyliques d'autre part: diacétyle, benzyle, glyoxal, dialdéhyde téréphtalique, dialdéhyde maléique, diacétyl-phényloxyde et sulfure de diacétyl-diphényle. La couleur des polymères obtenus variait du noir au gris. Les polymères étaient solubles dans le diméthylformamide et dans les acides acétique, formique et sulfurique. On a étudié les propriétés électriques des polybases de Schiff: la dépendance de la température suit l'équation $\sigma = \sigma_0 e^{-\Delta E/KT}$ et l'énergie d'activation varie de 3.6 à 0.8 ev; $\sigma_{20} = 10^{-13} - 10^{-11}$ ohms^{-1} cm^{-1}. Un certain nombre de composés possèdent une sensibilité photoélectrique. On a établi comment le photocourant dépendait du voltampère, du luxampère et de la température. On a aussi étudié le phénomène de polarisation dans le polymère produit par polycondensation de la benzyl- et de la *para*-phénylènediamine.

Zusammenfassung

Die Methode der linearen Polykondensation von Dicarbonylverbindungen mit Hydrazin oder seinen Salzen in organischen Säuren oder in Wasser-Alkoholmischungen mit Zusatz von Alkalihydroxyden als Katalysatoren wurde zur Darstellung einer Reihe von Polyazinen verwendet. Diese bilden gefärbte, verhältnismässig niedermolekulare Substanzen mit sehr geringer Löslichkeit in organischen Lösungsmitteln. Viele Polyazine besitzen eine kristalline Struktur. Ihr Widerstand besitzt eine exponentielle Temperaturabhängigkeit; die Aktivierungsenergie liegt im Bereich von 1,56 bis 2,82 EV und die spezifische Leitfähigkeit σ_{20} im Bereich von $7{,}08 \times 10^{-12}$ bis $1{,}12 \times 10^{-18}$

Ohm^{-1} cm^{-1}. Eine Reihe Schiff'scher Polybasen mit einem System konjugierter Doppelbindungen wurde aus *p*-Phenylendiaminen und 2,6-Diaminopyridin mit folgenden Carbonylderivaten dargestellt: Diacetyl, Benzil, Glyoxal, Terephthaldialdehyd, Maleindialdehyd, Diacetylphenoxyd und Diacetyldiphenylsulfid. Die Farbe der gebildeten Polymeren war schwarz bis grau. Die Polymeren waren in Dimethylformamid, Essigsäure, Ameisensäure und Schwefelsäure löslich. Die elektrischen Eigenschaften Schiff'scher Polybasen wurden untersucht: die Temperaturabhängigkeit gehorcht der Beziehung $\sigma = \sigma_0 e^{-\Delta E/KT}$ und die Aktivierungsenergie liegt zwischen 3,6 und 0,8 EV; $\sigma_{20} = 10^{-18}$ bis 10^{-11} Ohm^{-1} cm^{-1}. Bei einer Reihe von Verbindungen wurde photoelektrisches Verhalten festgestellt. Voltampère-, Luxampère- und Temperaturabhängigkeit des Photostromes wurden ermittelt. Am polymeren Produkt der Polykondensation von Benzil und *p*-Phenylendiamin wurde die Polarisationserscheinung untersucht.

Discussion

J. Jozefowicz (*Ecole de Physique et Chimie, Paris, France*): Je voudrais poser une question au sujet des spectres U.V. des solides qui sont donnés dans la communication. Comment ces spectres ont-ils été obtenus?

V. A. Kabanov (*Universite de Moscow, U.R.S.S.*): Je n'ai pas de détails expérimentaux sur ce travail qui a été fait par d'autres et que je présente seulement.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1315–1326

Synthesis and Some Electrophysical Properties of Polymers with System of Conjugated Bonds

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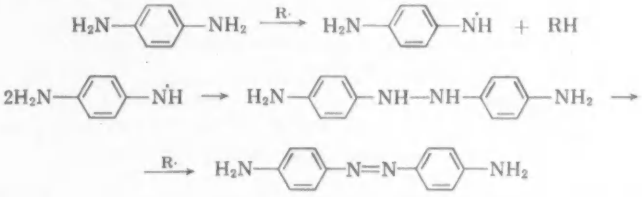
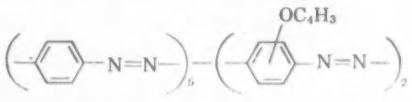
Polymers with a system of conjugated bonds were obtained by using new synthetic methods, reactions of polyrecombination and oxidative polydehydrocondensation.

The polyrecombination[1,2] is effected by decomposing organic peroxides in saturated compounds in liquid phase at a sufficiently high temperature for a fast decomposition of peroxide. The tertiary butoxyl and methyl radicals formed attack the solvent molecules, abstracting the most labile hydrogen atoms. The solvent radicals recombine to yield a polymer.

The synthesis of such polymers from aromatic amines, such as *p*-phenylenediamine, whose free radicals abstract primarily the most labile hydrogen atoms of the amino group[3] may be represented by the following scheme, where R is $(CH_3)_3CO\cdot$ or CH_3:

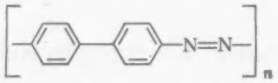


On the other hand, the growth of the chain pictured in eqs. (1) above is accompanied by butoxyl groups partially entering phenylene rings. Hence the following structure of a polyazobenzene polymer accounts most closely for the elementary analysis and infrared evidence:



The infrared spectra of this polymer as well as those of benzidine polymer reveal intensive absorption at 1270–1230 cm.$^{-1}$ characteristic of the stretching vibrations of the C—O group in arylalkyl ethers due to the tertiary butoxyl group.

Similarly, benzidine gives rise to polyazodiphenylene, also with a partial



substitution of hydrogen by butoxyl groups. These polymers are black, nonflammable powders which do not soften up to 650°C., are soluble in dimethylformamide, and have molecular weights of 5000–7000 (estimated isopiestically).

Conjugation of π-electrons of the azo group with π-electrons of the phenylene rings is exhibited by these polymers as well as similar ones (see Table I), revealing a narrow range ESR signal of a magnitude about 10^{18} electrons/g. (see Fig. 1) and a g factor of 2 (as with all similar polymers).

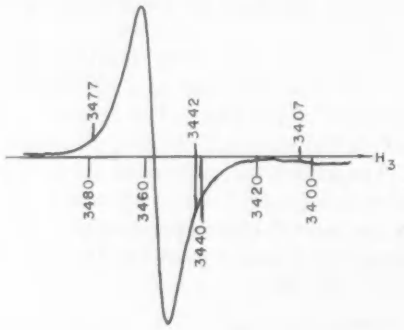
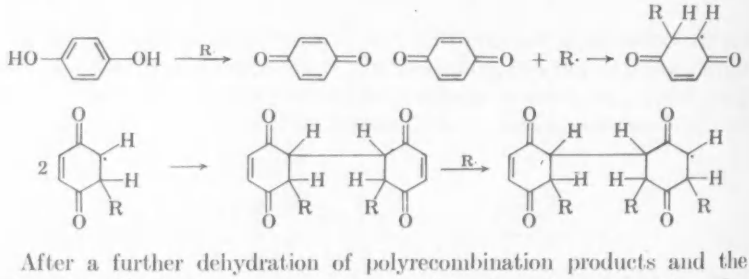
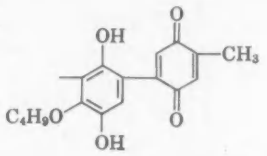


Fig. 1. ESR signal of *p*-phenylenediamine polymer.

The more intense ESR signal shown by the hydroquinone polymer seems to be due to the recombination of alkylated semiquinone radicals (similar to that of *p*-cresol radicals[4]) according to the scheme:



After a further dehydration of polyrecombination products and the migration of hydrogen to oxygen atoms in the polycyclic systems, the polymeric chain consists of alternating alkylated hydroquinone and quinoid rings. The results of elementary analysis, infrared spectra, and NMR data corresponds most closely to the following structure:



The quinoid structure in the infrared spectrum of the polymer (Fig. 2) is indicated by the intense absorption at 1670 cm.$^{-1}$, and the absorption at 1270 cm.$^{-1}$ is characteristic of alkyl aryl ethers. The hydroxyl group is revealed by the band at 3200–3400 cm.$^{-1}$ (OH at the hydrogen bond) and 3580 cm.$^{-1}$ (for the free hydroxyl group).

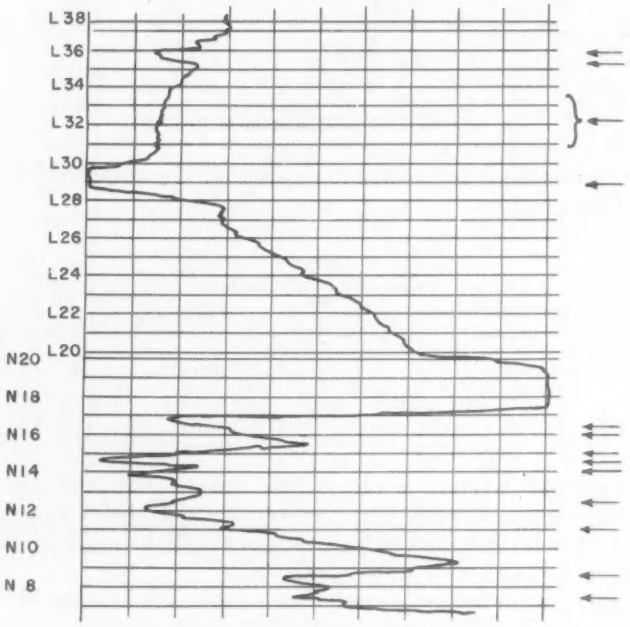


Fig. 2. Infrared spectrum of hydroquinone polymer.

The NMR spectrum of a 20% polymer solution in dimethylformamide shows a chemical shift from benzene of 7.9 $\times$ 10^{-7} (protons of phenol and quinoid rings) and 67.9 and 68.9 $\times$ 10^{-7} (protons of methyl group-linked quinone rings).

The hydroquinone polymer is a black powder, soluble in dimethylformamide; its molecular weight is about 10,000 and it softens at about 500°C. The polymer gives a narrow range signal (5 oersted width) and the intensity of its ESR signal N of a magnitude about 10^{20} electrons/g. (Fig. 3), is seemingly due to the quinoid structure in the polymer chain.

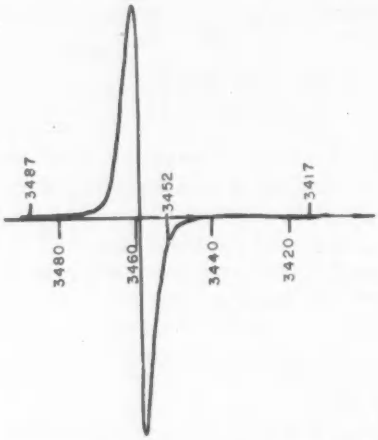
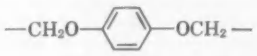
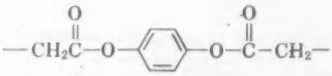


Fig. 3. ESR signal of hydroquinone polymer.

In this connection it is essential to note that the hydroquinone polymer ethers of the structure

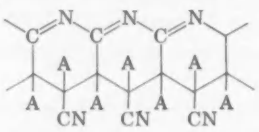


or



with no quinoid structure reveal no ESR signal. The properties of a number of hydroquinone copolymers with amines and other compounds are shown in Table I. Polymers with a system of conjugated —C=N— bonds have also been produced from fatty acid nitriles.

The chain growth induced by polyrecombination is accompanied by the polymerization of nitrile groups to give a system of —C=N— conjugated bonds in the sterically most favorable six-membered cycles. The methyl cyanoacetate gives rise to polymer of the type:



where A is —$COOCH_3$.

The infrared spectrum of the polymer revealed absorption bands characteristic of —C=N— bonds as well as of the nitrile and ester groups.

The polymer produced from malonitrile showed an exponential dependency of the specific resistance ρ on temperature (Fig. 4).[5] This permitted the energy of activation to be calculated as $E = 1.02$ e. v. and gave values for the specific conductance at 0°C., as $\sigma_0 = 4.37 \times 10^{-12}$ ohm^{-1} cm.$^{-1}$ and $\sigma_{20} = 2.32 \times 10^{-11}$ ohm^{-1} cm.$^{-1}$.

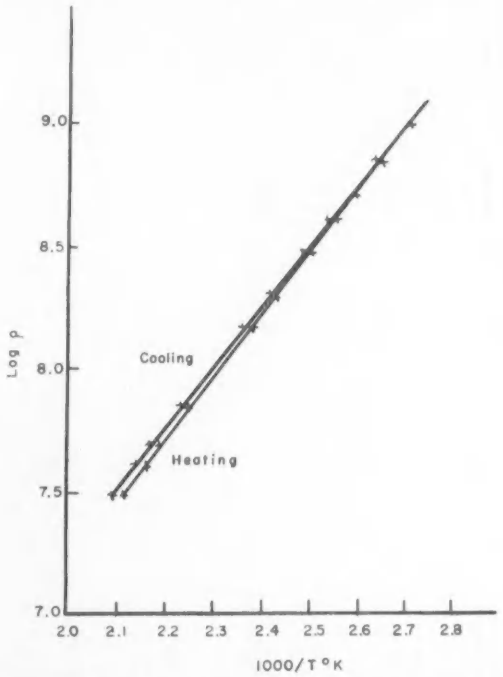


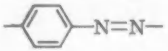
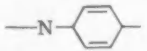
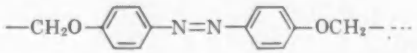
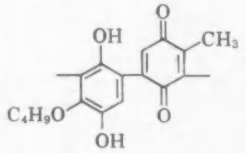
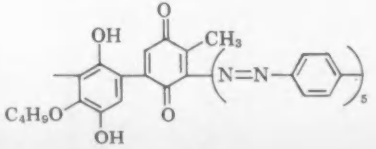
Fig. 4. Dependency of the specific resistance ρ on temperature for the malonitrile polymer. $E = 1.02$ e.v.; $\sigma_0 = 5.37 \times 10^{12}$ ohm^{-1} cm.$^{-1}$; $\sigma_{20} = 2.32 \times 10^{11}$ ohm^{-1} cm.$^{-1}$.

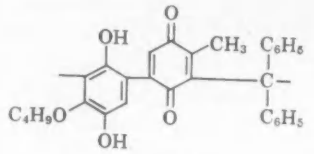
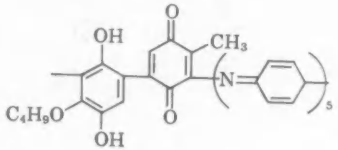
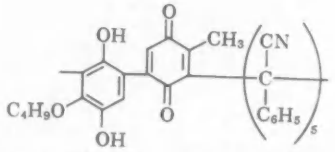
To synthesize polymers involving conjugated triple bonds in the chain we made use of the oxidative polydehydrocondensation reaction of acetylene compounds by the following scheme:[6,7]

$$x\,HC{\equiv}CH \rightarrow [-C{\equiv}C-]_x + 2xH^+$$

This reaction yielded polymers from acetylene, *p*-diethynylbenzene, 9,10-diethynyl-9,10-dihidroxydihydroanthracene, α,α'-dimethyl-β,β'-diethynylpyridine as well as their mutual copolymers and those with acetylene.[8] The infrared absorption data and the X-ray and elementary analysis data have shown these polymers to contain triple bonds and to be of the structure shown in Table II.

TABLE I
Polymers Involving Conjugated Bonds Prepared by Polyrecombination

Starting compound(s)	Suggested structure of polymers	Molecular weight	Softening temp., °C.	ESR data: Width of the signal, oersted	ESR data: Intensity of the signal electrons/g.
p-Phenylenediamine		7,000	650	9	1×10^{18a}
Benzidine		4,800	650	9	1×10^{18b}
Aniline		1,500	192	7	5×10^{17}
p-Anisidine		3,800	118	8	3×10^{18}
Hydroquinone		9,700	500	5	10^{20c}
p-Phenylenediamine and hydroquinone		5,600	500	10	6×10^{18}

Hydroquinone and diphenylmethane		9,500	540	5	4×10^{18}
Hydroquinone and aniline		—	140	9	9×10^{18}
Hydroquinone and benzyl cyanide		5,000	550	7	2×10^{18}

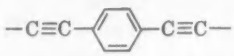
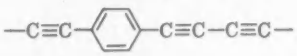
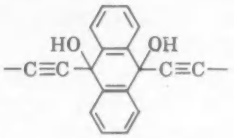
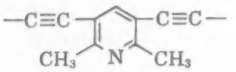
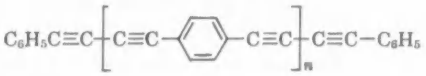
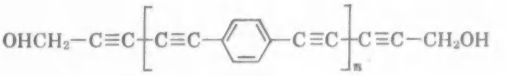
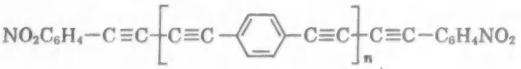
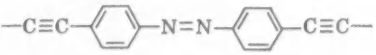
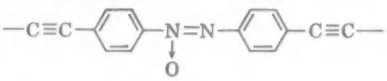
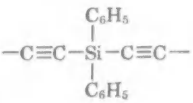
(continued)

TABLE I (*continued*)

Starting compound(s)	Suggested structure of polymers	Molecular weight	Softening temp., °C.	ESR data	
				Width of the signal, oersted	Intensity of the signal, electrons/g.
Methyl cyanoacetate	(A = —C(=O)—OCH$_3$)	7,200	500	7	1×10^{18}
Adiponitrile	(A = –(CH$_2$)$_4$CN)	11,000	110	8	3×10^{17}
Malonitrile		5,600	500	5.6	1.4×10^{19}[d]
Ferrocene		50,000	400	120	5×10^{21}[e]

[a] After thermal treatment at 500°C. the signal intensity $N = 10^{19}$ electrons/g. $E = 1.00$ e.v. (before thermal treatment).
[b] $E = 0.91$ e.v.; $\delta_{20} = 1.62 \times 10^{-16}$ ohm^{-1} cm.$^{-1}$
[c] $E = 2.1$ e.v.; $\delta_{20} = 9.3 \times 10^{-19}$ ohm^{-1} cm.$^{-1}$
[d] Activation energy of conductance $E = 1.02$ e.v.; specific conductance at 20°, $\delta_{20} = 10^{11}$ ohm^{-1} cm.$^{-1}$
[e] $E = 0.957$ e.v.; $\delta_{20} = 10^{-8}$ ohm^{-1} cm.$^{-1}$

TABLE II
Polymers Prepared by Oxidative Polydehydrocondensation

Starting substances	Structure of repeating unit of polymer
Acetylene	
p-Diethynylbenzene	
p-Diethynylbenzene and acetylene	
9,10-Diethynyl-9,10-dihydroxy-dihydroanthracene	
α,α'-Dimethyl-β,β'-diethynyl-pyridine	
p-Diethynylbenzene and phenylacetylene	
p-Diethynylbenzene and propargyl alcohol	
p-Diethynylbenzene and *p*-nitrophenylacetylene	
Dipropargylsulfone	
Dipropargylamine	
Diethynylazobenzene	
Diethynylazoxybenzene	
Diphenyldiethynylsilane	

The polymers are colored (dark yellow to black), powdered, and as a rule almost insoluble substances. To obtain soluble products we have carried out polydehydrocondensation of bis-acetylenic compounds with such terminators of the propagating chain as phenylacetylene, ethylacetylene, *p*-nitrophenylacetylene, propargyl alcohol, and methylethynylpyridine.

The polymers are soluble in benzene, alcohol, tetrahydrofuran, and ether, they are brightly colored and their molecular weight does not exceed 1000.

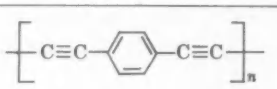
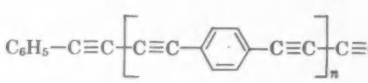
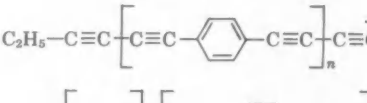
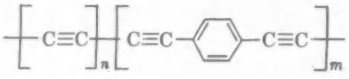
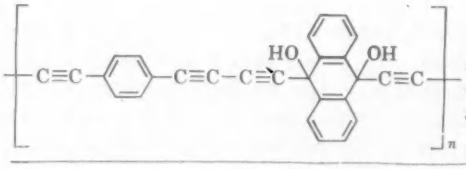
This reaction has also been used to prepare polymers containing heteroatoms together with a triple bond in the chain[9,10] (Table II).

The investigation of the electrophysical properties of carbochain polymers involving triple bonds in the chain has shown that they may be considered to be semiconductors. The specific resistance of these polymers was measured by the condensator discharge of the starting polymers and for their thermal treatment products by the penetration procedure. The temperature dependence was used to determine the energy of the conductance activation. With some polymers the thermal electric driving force was estimated (Table III).

Polymers prepared by the oxidative polydehydrocondensation of *p*-diethynylbenzene, acetylene, diethynyldihydroxydihydroanthracene and diethynylazobenzene were found in the laboratory of A. N. Terenin to be highly photoelectrically sensitive.[11] The spectral sensitivity for the photoconductivity and the photo-e.m.f. increases from the visible to the ultraviolet. Preliminary irradiation of the polymers by ultraviolet light en-

TABLE III

Electrophysical Properties of Polymers with Triple Bonds

Compound	Temp., °C.	Specific resistance, ohm cm.	Energy of activation of semiconductance e.v.	Thermal electric driving force, μv./°C.
	20	3.5×10^{13}	0.92	
	400	2.4×10^{12}	1.52	
	600	7.8×10^{7}	0.64	
	20	4.7×10^{13}	0.62	
	400	6.6×10^{13}	0.88	
	600	7.9×10^{10}	0.80	
	800	2.39	0.08	+15.5
	20	3×10^{14}	0.80	
	400	1.7×10^{13}	0.92	
	800	0.59	0.085	+4.0
	20	3.6×10^{14}		
	400	9.6×10^{12}	0.94	
	600	1.2×10^{12}	0.80	
	20	5.2×10^{13}	0.76	
	400	1.0×10^{13}	1.12	
	600	6.3×10^{9}	0.64	
	800	1.73	0.096	+6.5

hances the sensitivity in the visible. The dominant photocurrent carriers are positive holes and its decay is bimolecular. It is to be noted that of 100 various polymers studied in this laboratory, those with the triple bonds have been exceptionally active.

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11. Mylnikov, V. S., A. M. Sladkov, Yu. P. Kudryavzev, L. K. Luneva, V. V. Korshak, and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **144**, 840, (1962); V. S. Mylnikov, *Dokl. Akad. Nauk SSSR*, in press; V. S. Mylnikov, E. K. Putzeiko, and A. N. Terenin. *Dokl. Akad. Nauk SSSR*, in press.

Synopsis

Polymers with a conjugated system of carbon–nitrogen and carbon–carbon bonds have been obtained by the treatment of aliphatic and aromatic nitriles, aromatic diamines, and diphenols with *tert*-butyl peroxide (polyrecombination reaction). By this reaction polymers containing iron (polyferrocene) and germanium have also been obtained. Polymers and copolymers with conjugated system of carbon–carbon and carbon–other element bonds have been obtained from acetylene and bis-ethynyl derivatives of silicon, germanium, and tin by the oxidative polydehydrocondensation reaction. In the polymers with a conjugated system of bonds thus obtained the presence and the intensity of a single line of the ESR spectrum were determined to be due to the electron delocalization along the chain; the dependence of the electric conductivity on the temperature has been shown to have an exponential character. The values of the activation energy for conductivity and magnetic susceptibility were determined. The data obtained indicate that the polymers studied have some properties characteristic of semiconductor materials.

Résumé

On a obtenu des polymères possédant un système conjugué de liaisons carboneazote et carbone–carbone, en traitant des nitriles aliphatiques et aromatiques, des diamines aromatiques et des diphénols avec le peroxyde de *tert*-butyle (réaction de polyrecombinaison). C'est aussi par une réaction semblable que les polymères contenant du fer (polyferrocène) et du geramnium, ont été synthétisés. Les polymères et les copolymères possédant des systèmes conjugués de liaisons carbone–carbone et carbone–élément sont obtenus en partant d'acétylènes et de dérivés bis-éthyvinyliques du silicium, du ger-

manium et de l'étain, par une réaction de polydéhydrocondensation oxydante. On trouve que, pour les polymères aux liaisons conjuguées, la présence et l'intensité d'un singulet dans le spectre ESR est due à la délocalisation èlectronique le long de la chaîne, et on montre que la conductivité électrique dépend de 'a température selon une relation exponentielle. Les valeurs de l'énergie d'activation pour la conductivité et pour la susceptibilité magnétique sont déterminées. Les données obtenues permettent do constater que les polymères étudiés possèdent certaines propriétés caractéristiques des semi-conducteurs.

Zusammenfassung

Durch Behandlung aliphatischer und aromatischer Nitrile, aromatischer Diamine und Diphenole mit *tert*-Butylperoxyd (Polyrekombinationsreaktion) wurden Polymere mit konjugierten Systemen von Kohlenstoff-Stickstoff- und Kohlenstoff-Kohlenstoff-Bindungen hergestellt. Mittels dieser Reaktion wurden auch Polymere hergestellt, die Eisen (Polyferrocen) und Germanium enthalten. Aus Acetylen und Bis-äthinyl-Derivaten von Silicium, Germanium und Zinn wurden durch oxydative Polydehydrokondensation Polymere und Copolymere mit konjugierten Systemen von Kohlenstoff-Kohlenstoff- und Kohlenstoff-Element-Bindungen hergestellt. An den so hergestellten Polymeren mit konjugierten Bindungssystemen wurde das Auftreten einer einzigen, auf die Elektronendelokalisierung längs der Hauptkette zurückgehenden Linie im ESR-Spektrum festgestellt und ihre Intensität gemessen. Ausserdem wurde die exponentielle Natur der Temperaturabhängigkeit der eletrischen Leitfähigkeit nachgewiesen. Es wurde die Aktivierungsenergie für die Leitfähigkeit und die magnetische Suszeptibilität bestimmt. Wie aus den ermittelten Daten hervorgeht, haben die untersuchten Polymeren gewisse für Halbleiter charakteristische Eigenschaften.

Discussion

P. Teyssie (*Institut Français du Pétrole, Rueil-Malmaison, France*): We have shown that the reaction of molten benzoquinone with small amounts of polyisoprene yields a black polymer, containing a high number of spins (2.10^{21}); the structure of this semi-conducting product is not yet fully elucidated, but could be similar to that of the polyhydroquinone described here. The catalytic properties of these products are described elsewhere.

B. Eroussalimsky (*Léningrad, U.R.S.S.*): J'ai présenté seulement la communication, je ne dispose pas des éléments nécessaires pour répondre.

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Conductance Mechanism in Organic Semiconductor Polymers

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For the purpose of elucidating the mechanism of electrical conductivity in heat-treated polyacrylonitrile a study was made at an earlier date[1] of the temperature dependences of its resistance and thermal emf, the measurements being effected in the air on samples which differed both in temperature and medium of thermal conversion. The samples studied were either compressed tablets or fabrics. As a result of these investigations we arrived at the conclusion that the temperature dependence of the resistance is determined by the exponential temperature dependence of the mobility at constant current carrier concentration. Thereupon, as with all polymers studied up till now, the sign of the current carriers in the heat-treated polyacrylonitrile, determined by the sign of the thermal emf, was positive. Later,[2] adsorbed gases were found to have a strong influence on the conductance and the conductance activation energy values of the heat-treated polyacrylonitrile, consisting in a lowering of the resistance of the samples when heated *in vacuo*.

In this work a systematic investigation was undertaken in 5×10^{-1} mm. Hg vacuum of the temperature dependences of the resistance and thermal emf on fiber samples of heat-treated polyacrylonitrile differing only in their treatment temperatures.

Figures 1 and 2 show characteristic temperature dependences of the resistance and thermal emf of several samples of polyacrylonitrile samples subjected to heat treatment at different temperatures. Table I presents values of the specific resistance ρ and thermal emf α relative to lead taken at 100°C. for all the samples under study with treatment temperatures ranging from 520 to 730°C. measured before and after heating the samples *in vacuo*. As is evident from the figures and from the table, the first heating of the samples *in vacuo* to 420°C. results in an irreversible change in the resistance and the thermal emf, the resistance decreasing approximately threefold in the case of the sample treated at 730°C. and tenfold in the case of that treated at 520°C. The effect of heating *in vacuo* on the thermal emf is still greater. In the case with all samples, except that treated at 730°C., the thermal emf changes its sign, i.e., samples with *p*-

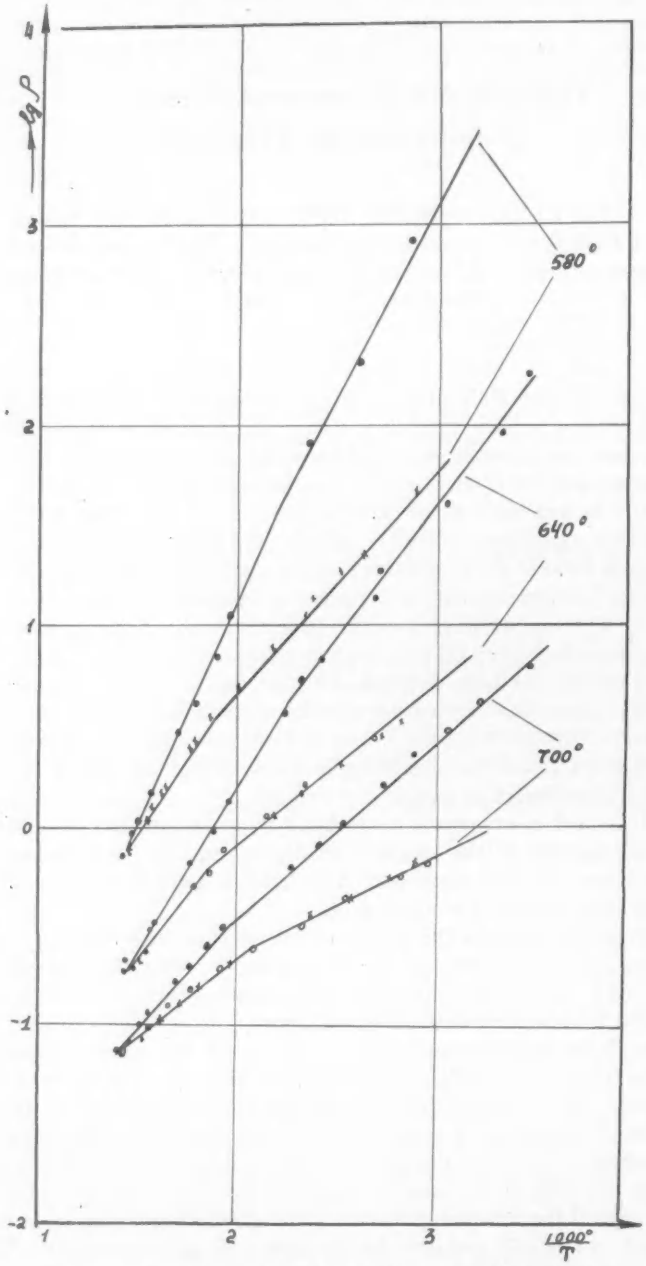

Fig. 1. Dependence of the specific resistance on temperature.

type conductivity in the air are found to have *n*-type conductivity after heating *in vacuo*. A second heating of the samples *in vacuo* to 420°C. changes the resistance and thermal emf reversibly. We attribute the drop in resistance of heat-treated polyacrylonitrile and the change in sign of the

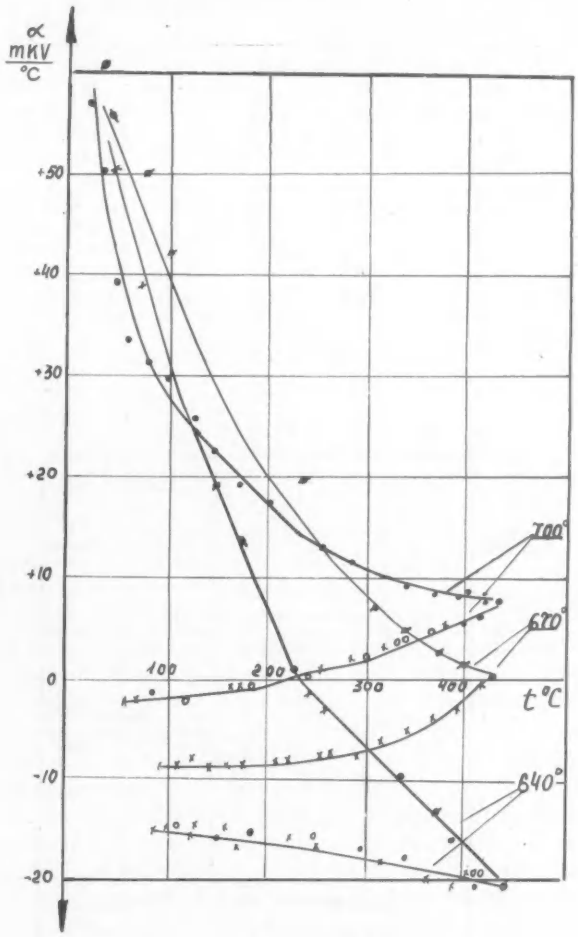

Fig. 2. Dependence of the thermal emf on temperature.

current carriers from positive to negative (according to the sign of the thermal emf) as a result of heating *in vacuo* to gas desorption. This is borne out by the fact that when the degassed samples are brought out into the air their resistance regains its original value, while the thermal electromotive force again becomes positive.

TABLE I

Specific Resistance ρ and Thermal emf α Before and After Heating *in vacuo*

Treatment temperature, °C.	Specific resistance, ohm-cm.		Thermal emf, μv./°C.		Temperature at which $\alpha = 0$, °C.
	Before heating ρ_1	After heating ρ_2	Before heating α_1	After heating α_2	
520	4.6×10^3	4.6×10^2	—	−104	—
580	2.9×10^2	25	—	−42	—
600	3.3×10^2	46	—	−48	—
620	40	5.5	—	−22	—
640	18	3.8	—	−17	—
640	17	2.9	+88	−15	—
670	4.2	1.5	+61	−8.8	425
680	1.8	0.5	+54	−4.8	410
700	1.4	0.48	+45	−2	235
710	0.37	0.15	+36	−0.4	120
730	0.42	0.15	+26	+0.7	—

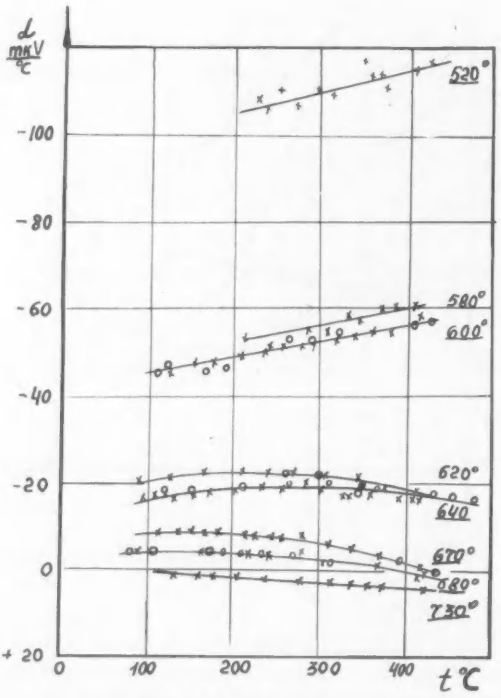

Fig. 3. Dependence of the thermal emf on temperature.

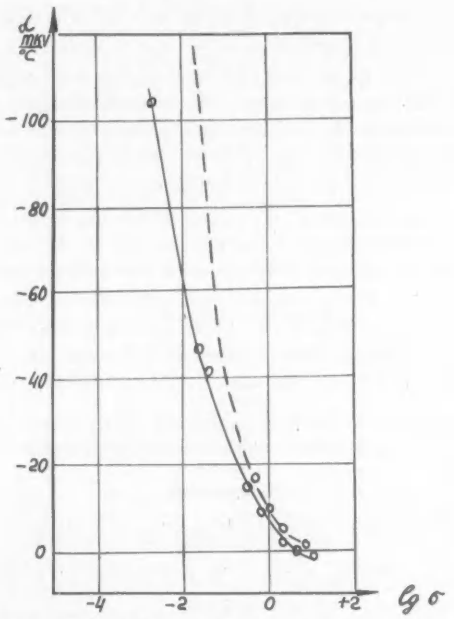

Fig. 4. Dependence of the thermal emf on log conductivity.

Figure 3 shows the temperature dependences of the thermal electromotive force of samples heated preliminarily *in vacuo* at 5×10^{-6} mm. Hg for several hours at a maximum temperature of 420–440°C., i.e., degassed to such an extent that their temperature resistance and thermal emf dependences have become fully reversible. It can be seen from this figure that the thermal emf of samples treated at low temperatures (520, 580, and 600°C.) increases linearly with the temperature rise. Samples treated at high temperatures (670, 680, 700, and 710°C.) have not a very large thermal emf value at room temperature, which drops to zero as the temperature of measurement rises and becomes positive and then grows somewhat at further rise of the temperature. For these samples Table I shows the temperature at which the thermal emf becomes zero. The temperature dependence of the thermal emf of the degassed samples, we believe, testifies to the fact that the current carriers in the substances studied are in a state of either complete or partial degeneration, their concentration being independent of the temperature, and therefore the exponential decrease in resistance due to a temperature rise, as is the case with the *p*-type samples, when measured in the air, is determined by the exponential increase in the effective mobility of the current carriers.

The assumption as to the degeneration of the current carriers in the samples under study is also confirmed by the type of thermal emf versus electrical conductivity dependence corresponding to a temperature of

100°C. for all the samples studied (see Fig. 4). For the sake of comparison Figure 4 also contains the theoretical curve of thermal emf versus conductivity dependence, plotted on the basis of the most general expression for the thermal emf[3] as a function of the concentration for any concentration of current carriers of one sign with allowance for the following assumptions: (*a*) the effective mobility of the current carriers remains unchanged with increasing treatment temperature and is the same for all samples; (*b*) the free run of the carriers is independent of the energy.

One point, corresponding to a mobility of 1.3×10^3 cm.^{2}/v.-sec. if the effective mass of the carriers is assumed to be equal to the mass of a free electron, coincides on the theoretical and experimental curves. As is evident from Figure 4, the theoretical curve is steeper than the experimental one. This apparently testifies to the fact that the mobility of different samples is different and increases with the treatment temperature rise.

In conclusion we wish to express our gratitude to L. S. Stilbans for the constant interest in our work and for the help rendered in discussing the results.

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Synopsis

A previous study of the dependence of differential thermal emf and temperature showed that the character of this dependence is governed by the nature of the polymer when experiments are conducted in air. The present paper describes how the adsorption of oxygen influences the electrophysical properties of semiconducting materials derived from polyacrylonitrile. The desorption of oxygen is accompanied by an increase in conductivity and by a decrease in the energy of activation of polymeric semiconductors. The desorption of oxygen is also accompanied by a decrease in thermal emf (positive sign) which at definite temperatures characteristic of each semiconductor passes through zero and changes its sign. The desorption of oxygen thus causes the transition of the hole-containing semiconductor (as the sign of thermal emf shows) into electronic materials. The dependence between the thermal emf of deaerated polymeric semiconductors and temperature indicates the existence in the studied examples of partially or completely degenerated current carriers; their concentration does not depend on the temperature, and the exponential increase of conductivity is determined by exponential increases of the efficient mobility of the carriers. Moreover, the assumption that carriers degenerate is confirmed by the nature of the dependence between the thermal emf and electroconductivity.

Résumé

L'étude de la dépendance de la emf-thermique différentielle vis-à-vis de la température, a montré que le caractère de cette dépendance est gouvernée par la nature du polymère quand las expériences sont effectuées à l'air. Cet article décrit comment l'adsorption d'oxygéne influence les propriétés électrophysiques des semiconducteurs dérivés du polyacrylonitrile. On a montré que la désorption d'oxygène est accompagnée d'une augmen-

tation de a conductivité et d'une diminution d'énergie d'activation des semiconducteurs polymériques. La désorption d'oxygène est également accompagnèe d'une diminution dans la thermo-emf (signe positif) laquelle à des températures caractéristiques pour chaque semiconducteur passe par zéro et change de signe. La désorption d'oxygène est alors cause de la transition du semiconducteur qui contient des lacunes (comme le montre le signe de la thermo-emf) en matériel électronique. La dépendance entre la thermo-emf des semiconducteurs polymériques déaérés et la température indique l'existence dans les exemples étudiés de supports de courant partiellement ou complètement dégénérés; leur concentration est indépendante de la température et la croissance exponentielle de la conductivité est déterminée par l'augmentation exponentielle de la mobilité efficace des supports. De plus l'hypothèse de la dégénérescence des supports est confirmée par la nature de la dépendance entre la thermo-emf et l'électroconductivité.

Zusammenfassung

Bei der Untersuchung der Temperaturabhängigkeit der differentiellen Thermo-EMK wurde gefunden, dass bei der Durchführung der Versuche in Luft die Art dieser Abhängigkeit durch die Natur der Polymeren bestimmt wird. In der vorliegenden Arbeit wird der Einfluss der Sauerstoffadsorption auf die elektrophysikalischen Eigenschaften der von Polyacrylnitril abgeleiteten Halbleitermaterialien beschrieben. Die Desorption von Sauerstoff wird von einer Zunahme der Leitfähigkeit und einer Abnahme der Aktivierungsenergie der Polymerhalbleiter begleitet. Bei der Desorption von Sauerstoff nimmt ausserdem die Thermo-EMK (positives Vorzeichen) ab, wird bein einer definierten, für jeden Halbleiter charakteristischen Temperatur Null und wechselt das Vorzeichen. Wie das Vorzeichen der Thermo-EMK zeigt, bewirkt also die Sauerstoffdesorption den Übergang von einem Lochhalbleiter in ein elektronisches Material. Die Temperaturabhängigkeit der Thermo-EMK luftfreier Polymerhalbleiter weist bei den untersuchten Beispielen auf die Existenz partiell oder vollständig entarteter Stromträger hin. Ihre Konzentration ist von der Temperatur unabhängig und das exponentielle Ansteigen der Leitfähigkeit wird durch die exponentielle Zunahme der effektiven Beweglichkeit der Träger bestimmt. Die Annahme einer Entartung der Träger wird ausserdem durch die Art des Zusammenhanges zwischen Thermo-EMK und elektrischer Leitfähigkeit gestützt.

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Conducting Polymers from Cyclopentadiene

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INTRODUCTION

Cyclopentadiene readily forms low molecular weight thermal polymers that are considered to be Diels-Alder type addition products. Low molecular weight, colored polymers are produced when cyclopentadiene is polymerized by trichloroacetic acid.[1] These polymers have a molecular weight of about 1000; they are blue as originally prepared in the protonated form and change to red-brown when the proton is removed. Cyclopentadiene can also be polymerized by $SnCl_4$[2] and the combination of $TiCl_4$ and $Al[CH_2CH(CH_3)CH_3]_3$[3] to give polymers with a molecular weight of about 30,000 which are white in color. Wassermann[1] has shown that solutions of the low molecular weight polymers conduct electricity and the chromophore is conjugated unsaturation occurring in the polymer chain. This paper deals with the structure of the high molecular weight polymer and some unusual properties associated with a reaction product of this polymer.

RESULTS

Polymerization

Monomer was prepared by cracking dimer over hot oil; it was stored under nitrogen atmosphere at Dry Ice temperatures.[4] Since metal alkyls and transition metal halides were used as catalysts, solvents, reagents, and glassware had to be dry and free from oxygen. Polymerizations were conducted in round glass bottles sealed with serum caps; solvent, catalyst, and monomer were injected through the cap. After the required interval, the contents of the flask were poured into a large excess of methanol. White polymer precipitated, was collected by filtration, and dried in vacuum at 50°C. At this point, polymer was ready for further experimentation. Reaction conditions for a number of polymerizations are listed in the first five columns of Table I. Detailed studies in toluene showed that there is definite and opposite temperature dependence exhibited by both catalysts. Yield of polymer is highest at −70°C. and decreases as the temperature increases when $TiCl_4$ alone is used as a catalyst. When Ziegler-type catalyst is used, the yield increases as the temperature is raised from −70 to 0°C.

TABLE I
Bromination and Dehydrobromination of Polycyclopentadiene
Bromine Content Resulting from Variation in Reaction Conditions

Solvent[a]	Catalyst	Temp., °C.	Time, hr.	Yield, %	Bromine, %
Toluene	$TiCl_4$[b]	−70	48	100	42.7
Toluene	$TiCl_4$ + TIBAL[c]	−70	48	17	41.2
Toluene	$TiCl_4$	0	17	70	41.2
Toluene	$TiCl_4$ + TIBAL	0	17	94	39.8
Toluene	$TiCl_4$	50	17	54	36.2
Toluene	$TiCl_4$ + TIBAL	50	17	82	34.6
Benzene	$TiCl_4$	50	17	53	38.3
Benzene	$TiCl_4$ + TIBAL	50	17	90	34.7
Cyclohexane	$TiCl_4$	50	17	12	—
Cyclohexane	$TiCl_4$ + TIBAL	50	17	64	36.1
Cyclohexane	$TiCl_4$ + TIBAL	50	1	27	—
$CHCl_3$	$SnCl_4$[c]	0	15[d]	96	37.4

[a] Solvent 200 ml., cyclopentadiene 10 ml.
[b] $TiCl_4$ solution 2.2 ml. (2.0 mmoles).
[c] $TiCl_4$ solution 2.2 ml.; TIBAL (triisobutylaluminum) 2.3 ml. (1.93 mmoles).
[d] Reaction time 15 min.

Bromination Studies: Qualitative

When bromine is added to solution of the polymer in either carbon tetrachloride or cyclohexane, a fascinating series of events takes place. Within seconds the bromine color disappears as it adds to the double bonds. In about 30 sec., the solution begins to pass through a series of color changes from yellow to yellow-green to green to a final blue-black; HBr gas is evolved simultaneously with the color change. Thus bromine acts as a dehydrogenating agent, and the color changes indicate that progressively longer sequences of conjugated unsaturation are being formed in the polymer.

A small amount of bromine was added to a carbon tetrachloride solution of the polymer, and the electronic absorption spectrum was studied over a period of time. The carbon tetrachloride solution of polymer does not absorb in the visible spectrum, but as Figure 1 indicates dehydrobrominated polymer does. There are three important characteristics of this curve: (1) absorption intensity in the entire visible region increases with time; (2) intensity is stronger at shorter wavelengths; (3) there are no discrete maxima in the curve.

Since the curves are smooth and no discrete maxima appear, no specific chromophore is present in much greater concentration than the others. A curve such as this can be attributed to polymers in which there are a

number of chromophores each having different absorption maxima at an ever increasing wavelength. This can readily come about in a polymer that has conjugated unsaturation with an ever increasing number of double bonds in the conjugated sequence. Such a curve would appear as a smooth integration of all the absorption maxima, and no maximum would appear separately unless one particular chromophore comprised of a specific

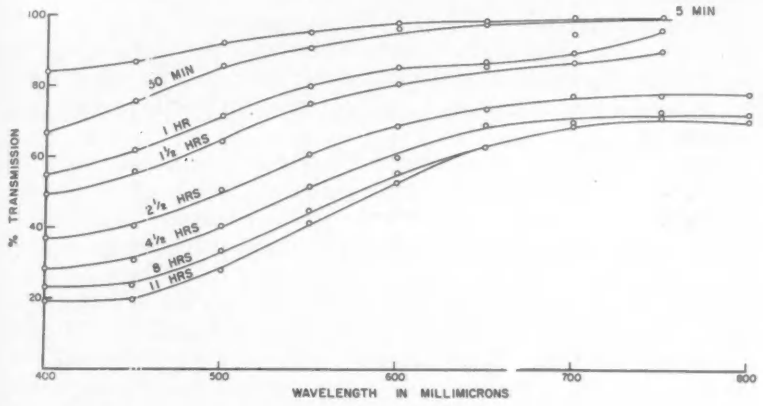


Fig. 1. Change in absorption of brominated polycyclopentadiene with time.

number of double bonds dominated the structure of the polymer. In a random process of bromination with no restrictions on dehydrobromination, the abundance of each chromophore would be expected to decrease as the length of conjugation in the chromophore increased.

Bromination Studies: Quantitative

For stoichiometric calculations, it was assumed that each five-membered ring in the polymer still retained one double bond, and enough bromine was added to have one mole for each mole of double bond. In an early experiment the bromination and dehydrobromination was conducted in an open vessel. After a short period of heating and stirring, a black precipitate formed that had the appearance of fine charcoal or carbon black. The bromine content of this polymer was 67.7%. This is very close to the maximum bromine content of 70.8%, the theoretical value for a polymer completely saturated with bromine. This showed that the polymer could take up its theoretical content of bromine.

The following experiments were performed in closed systems from which air and water were excluded. Prior to use, solvents were treated with dry nitrogen, and a continuous stream of dry nitrogen was supplied to the vessel during the dehydrobromination. Polycyclopentadiene dissolved in carbon tetrachloride was treated with a stoichiometric amount of bromine, and in certain experiments base was added after 1 hr. Following 20 hr. of re-

fluxing, polymer was collected by filtration, purified, and vacuum dried overnight.

In one experiment, two samples of polycyclopentadiene were treated identically except that in one case one mole of pyridine was added for each mole of bromine; while in the other, two moles of pyridine were added. The bromine remaining in the polymers was 39.8 and 38.2%, respectively. Two other samples were treated similarly except that equivalent amounts of tri-*n*-propylamine ($K_b = 5.5 \times 10^{-4}$) and pyridine ($K_b = 2.3 \times 10^{-9}$) were used. The bromine remaining in the polymer was 38.8 and 35.9%, respectively. It was concluded that neither increasing the amount nor strength of the base contributed to further removal of bromine as hydrogen bromide.

Bromine was added to a carbon tetrachloride solution of polycyclopentadiene and the reaction vessel was heated at reflux for 20 hr. without base having been added directly to the reaction mixture. A stream of nitrogen was swept through the solution, then through an ice trap to remove free bromine, and next into a trap with standard NaOH to remove the HBr. No bromine appeared in either trap nor was any left in the reaction vessel; thus all of it was involved in the reaction. The amount of HBr was determined, and from this the bromine content of the polymer was estimated to be 35.6%. The remaining bromine content from this experiment is roughly equal to that obtained from the previous experiments in which base was used. Apparently the amount of bromine remaining in the polymer is not affected by the method of removal, and it appears that in each case nearly the same experimental value is obtained. Some of the dry powder from the preceding experiment was pyrolyzed in nitrogen at a temperature of 235°C., and the gas stream was caught in standard NaOH as described previously. A small amount of HBr was liberated, and the remaining bromine content was reduced to 32%. This shows that there are two kinds of bromine present in the polymer: one that is removed readily and one that is very resistant to further reaction. The experimentally determined bromine contents are very close to 38.3%, which is the calculated value for one bromine atom for every two cyclopentadiene rings.

Bromine Content and Polymerization Conditions

Since two types of bromine are indicated, it was assumed that the difference in reactivity was a result of a difference in structure. We sought to change the structure of changing experimental conditions; Table I summarizes the experimental conditions and the results obtained. Four solvents, three catalysts, and three widely separated temperatures were used in these experiments, and in all cases the bromine content of the resulting polymers is very similar. If the bromine content of bromodehydropolycyclopentadiene is dependent on the structure of the original polymer, it has not been changed through broad changes in experimental conditions. The results indicate a preferred structure in which there is one bromine atom for every two five-membered rings.

Infrared Analysis

Infrared spectra were obtained from samples described in Table I. The spectra were strikingly similar, suggesting a similarity in the structure of the polymers. KBr pellets of the various polycyclopentadienes were prepared and showed absorption maxima corresponding to *cis*=C—H stretching at 3077 cm.$^{-1}$, C=C stretching at 1621 cm.$^{-1}$, CH_2 stretching at 2933 and 2865 cm.$^{-1}$, CH_2 deformation at 1451 cm.$^{-1}$, and CH deformation at 1364 cm.$^{-1}$. Thus infrared study confirms the presence of double bonds in polycyclopentadiene.

Bromodehydropolycyclopentadiene was formed into KBr pellets and the infrared spectrum showed maxima corresponding to =C—H stretching at 3049 cm.$^{-1}$, C = C stretching at 1623 cm.$^{-1}$, CH_2 stretching at 2933 and 2857 cm.$^{-1}$. Thus, as expected, the dehydrobrominated polymer showed evidence for the presence of double bonds.

Physical Properties of Bromodehydropolycyclopentadiene

The polymer has the appearance of carbon black or graphite; it is insoluble in common laboratory solvents in which it was tested, and it does not melt below 300°C. It is readily molded into various shapes by the application of pressure. Since the material resembles dehydrated polyvinyl alcohol and black polyacrylonitrile, it was expected to have unusual thermal and electrical properties.

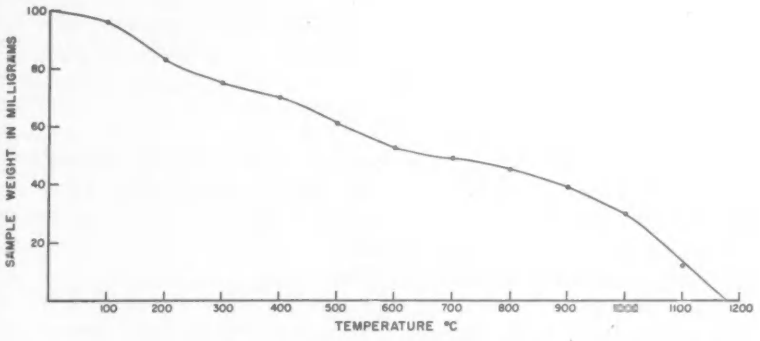


Fig. 2. Weight remaining vs. temperature for bromodehydropolycyclopentadiene (No. 56A-1) on pyrolysis on a thermogravimetric balance in a nitrogen atmosphere.

Figure 2 shows the results of pyrolysis of a 100 mg. sample of bromodehydropolycyclopentadiene in a nitrogen atmosphere. The sample was placed in a thermogravimetric balance and the heat was programmed to reach a temperature of 1200°C. in 1.5 hr. At 900°C. the polymer was still 50% intact and was not completely pyrolyzed until the temperature was beyond 1100°C. The results demonstrate the thermal stability imparted to the polymer by long sequences of conjugation.

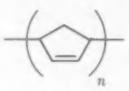
It has recently been shown by a number of workers[5] that enhanced electrical conductivity is dependent on the number of conjugated double bonds, or π- electrons, contained in polymers, and thus it seemed reasonable that bromodehydropolycyclopentadiene should have enhanced conducting properties. A die and press was used to mold the polymer into short cylinders which were clamped between two platinum electrodes. Resistance was measured with a 1000-cycle General Radio impedance bridge. Resistivities in the range of 10^6 ohm-cm. were obtained. This places this material in the semiconducting range. In addition the electron spin density was measured and found to be 10^{18} spins/g., which indicates an abundance of free radicals. These free radicals are unquestionably stabilized by the long sequences of conjugation.

DISCUSSION

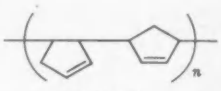
The foregoing studies have furnished evidence for the selection of the most probable structure of the original polymer polycyclopentadiene. Experimental results indicate there is one bromine atom and three double bonds for every two cyclic members in bromodehydropolycyclopentadiene; in addition there are long sequences of conjugation.

There are three ways in which cyclopentadiene can polymerize in a linear fashion and they are: all-1,2 (I); all-1,4 (II); and a combination of 1,2 and 1,4 (III). The all-1,2 structure can be ruled out

1,2
(I)



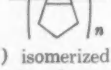
1,4
(II)



1,2–1,4
(III)

immediately by consideration of the bromine content and the implications of the isomerization reaction. The all-1,2 form need loose only one bromine from each ring to give a completely conjugated structure, and using this as a basis for calculation the bromine content would be 55.2%. This is in poor agreement with experimental values of 38%.

If an all-1,2 polymer were subjected to isomerization through treatment with acid, it would isomerize in such a fashion as to lead to a completely conjugated backbone (IV). However, this does not agree with experimental results; it has been shown[1] that the electronic spectrum of



(II) isomerized,
1,2 polymer
(IV)

isomerized polymer has an absorption maximum at 3650 A. which corresponds to a sequence of six conjugated double bonds. Thus a structure

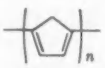
must be devised which logically limits the chromophore length in the isomerized polymer to about six double bonds.

The choice is between the all-1,4 or some combination of 1,2 and 1,4; and the evidence at hand does not allow the exclusion of either structure. From the standpoint of polymerization mechanism, the all-1,4 structure is favored. The polymerization of other 1,3-dienes such as butadiene, isoprene, and cyclohexadiene[6] (a cyclic diene similar to cyclopentadiene) has been studied. When these dienes are polymerized in a reaction catalyzed by Ziegler and certain cationic reagents, the polymer has the predominately 1,4 structure. Cyclopentadiene would be expected to do the same. Polymerization results listed in Table I show the bromine content remains the same in polymers that have been prepared under vastly different experimental conditions. If a random 1,2–1,4 arrangement is postulated, the amounts of 1,2 and 1,4 contained in the polymer would be expected to change considering the vast range of experimental conditions that were used.

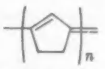
An alternate 1,2–1,4 arrangement would not be in accord with the results from the polymerization of other dienes. Alternate polymerization would require the formation of both the 1,2- and the 1,4-ions and suggest steric hindrance as the most probable reason for alternate addition. Construction of the molecular models does not indicate hindrance to 1,4 addition. Thus it is reasonable to favor all-1,4 addition over either random or alternate 1,2–1,4.

Structures containing one bromine atom and three double bonds for every two five-membered rings can be drawn for both the all-1,4 and the 1,2–1,4 arrangement. In addition, other structures can be proposed. The problem can be resolved to choosing the most probable structure for the 1,4 and the 1,2–1,4 arrangements, respectively, and comparing their bromine content with experimental values.

The resonance energy for butadiene is known to be 3.5 kcal./mole. In addition to the resonance energy, there is a conformational energy of 2.3 kcal./mole[7] between the cisoid and the transoid forms; the former being the higher energy conformation. Five-membered rings possessing two double bonds have the high energy cisoid conformation; as can be seen by comparing the 1.6 kcal./mole resonance energy of 1,3-cyclopentadiene with that of butadiene given above. Conjugating through an exocyclic double bond, which can assume the transoid conformation, would lower the energy requirement of the system and be the preferred arrangement (V).



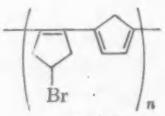
Endocyclic,
high energy



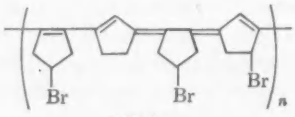
Exocyclic
low energy

(V)

Consider the 1,2–1,4 arrangements shown in (VIa) and (VIb).



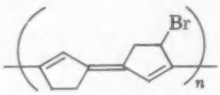
(VIa)



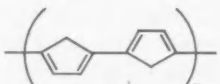
(VIb)

Structure (VIa) has a calculated bromine content of 38.3% and a completely conjugated structure; but it also has one cisoid bond out of three. Structure (VIb) represents a 1,2–1,4 arrangement with one less cisoid conformation. The cisoid bond that is present is exocyclic, and since it is not contained in a rigid ring system would be at a lower energy state than an endocyclic conformation. The bromine content of this structure is 48%, which does not agree with experimental values. If the polymer were in the 1,2–1,4 arrangement it would be expected to have a bromine content nearer the 48% value.

Formulas (VIIa) and (VIIb) show arrangements for the all-1,4 polymer.



(VIIa)



(VIIb)

Structure (VIIa) has a 38.3% bromine content, no cisoid dienes, and a completely conjugated backbone. The remaining bromine would be very stable, since its removal could only be brought about at the expense of the energy associated with the formation of two cisoid structures as shown in (VIIb). Therefore, it is reasonable to consider structure (VIIa) as the most stable for the 1,4 arrangement.

The driving force for the dehydrobromination is the resonance stabilization energy of the conjugated system. The dehydrobromination process can be visualized as starting with the formation of a cyclic bromonium ion which opens to give a carbonium ion. The carbonium ion would isomerize to a position of lowest energy, one of the tertiary carbon atoms along the backbone of the chain. Loss of a proton, of course, gives a double bond. A carbonium ion formed on a adjacent ring will isomerize until it is conjugated and stabilized by the first double bond. In this manner, a conjugated sequence proceeds down the chain.

As the conjugated system grows, the length of each single and double bond will converge to an intermediate value,[8] and greater delocalization of the π electrons will occur. Kuhn showed the following relationship could be applied to conjugated systems of double bonds:

$$\Delta E = (h^2/8mL^2)(N + 1)$$

where ΔE is the energy required for the excitation of one electron from the highest occupied to the lowest unoccupied orbital, L is the length of the un-

saturated sequence; N is the number of π-electrons; h is Planck's constant, and m is the mass of the electron. Thus the excitation energy is directly proportional to the number of π-electrons and inversely proportional to the square of the length of the unsaturated chain. Increasing the length of unsaturation should allow the electrons to become increasingly more mobile and cause an increase in the conductivity of the polymer. The resistivity for bromodehydropolycyclopentadiene, 10^6 ohm-cm., allows it to be classified as a semiconductor.

The observed thermal stability can be explained readily in terms of the increased stability imparted to the system by the resonance energy derived from the long sequences of conjugation.

EXPERIMENTAL

Monomer Preparation and Storage

Dicyclopentadiene was obtained from the Enjay Company Inc. and cracked according to their directions.[4] The monomer, cyclopentadiene, was stored under nitrogen in a serum capped bottle at Dry Ice temperature. Monomer, all solvents, and solutions of catalyst were transferred by means of hypodermic syringe.

Polymerization Solvents

Solvents were distilled from sodium under a nitrogen atmosphere and stored over molecular sieve in glass bottles with serum stoppers.

Catalysts

Titanium tetrachloride was prepared by injecting 45 ml. of dry cyclohexane and then 5 ml. of titanium tetrachloride into a glass bottle. Weights were taken and the concentration calculated (usually about 0.90 mmoles/ml.). Triisobutylaluminum was obtained from Texas Alkyls as a 25% solution in n-heptane and was used directly (calculated 0.840 mmoles/ml.).

Polymerization

Careful attention was devoted to maintaining dry conditions throughout all polymerization steps. Solvent (200 ml.) was injected into serum capped bottles. This was followed by 2.3 ml. of triisobutylaluminum solution and then 2.2 ml. of $TiCl_4$ solution. A deep brown precipitate formed immediately upon injection of $TiCl_4$; this complex was allowed to age for $^1/_2$ hr. before injection of monomer. Reaction vessels were brought to the proper temperature and monomer was injected. After the required reaction time, usually about 17 hrs., polymer was isolated by pouring the contents of the flask into methanol, previously gassed with dry nitrogen, while being vigorously stirred. The white precipitate was filtered and vacuum dried in an oven under a nitrogen atmosphere at 50°C. for 4 hr.

The preparation with $SnCl_4$ as a catalyst was conducted in a three-necked flask equipped with stirrer, condenser, and combination addition funnel and gassing tube. The flask was maintained at 0°C. and was purged continuously with nitrogen; first 200 ml. of $CHCl_3$ was added and then 25 ml. cyclopentadiene. $SnCl_4$ (2.18 g.) was added to 20 ml. of $CHCl_3$, and this solution was added dropwise over a period of 15 min. Pyridine (3 ml.) was added to precipitate the $SnCl_4$, and this precipitate was removed by filtration. Polymer was precipitated by adding the solution to a large volume of methanol. Polymer was collected and dried as given above.

Bromination of Polycyclopentadiene

Bromination was conducted in a three-necked flask equipped with an addition funnel, gas inlet tube, reflux condenser, magnetic stirrer, and heater. CCl_4 (100 ml.) was added to the flask and stirred, and a slow stream of nitrogen was allowed to flow throughout the entire reaction period. A 6-g. portion of polymer was added and dissolved rapidly in the CCl_4. Bromine (14.52 g.) was weighed into 50 ml. of CCl_4 and was added rapidly to the reaction mixture via the addition funnel. Bromine addition occurred immediately and polymer began to precipitate; at the same time, large quantities of HBr were evolved. After $^1/_2$ hr., 15.8 g. of pyridine was added rapidly via the addition funnel; heat was applied and the mixture was allowed to reflux overnight. The mixture turned black quickly after addition of the pyridine. After a 24-hr. reaction period, the product which had separated was isolated by filtration. Polymer was purified by slurrying several times in CCl_4 and then in methanol. The polymer was filtered after each slurry and was finally dried in vacuum overnight at 55°C.

Bromine Determination

Bromine was determined by reduction with sodium and ammonia and titration of the resulting bromide. Usually 200 mg. of bromodehydropolycyclopentadiene was added to about 20 ml. of liquid ammonia. A few pieces of sodium were added, and the samples needed only to be agitated until the ammonia evaporated. Water was added; the sample was filtered and adjusted to neutrality with HNO_3 and titrated with 0.05*N* $AgNO_3$ solution. The endpoint was determined potentiometrically with a pH meter and calomel, silver, silver bromide electrodes.

I wish to thank the Socony Mobil Oil Company, Inc., for the opportunity to pursue this research and to prepare this paper. Special acknowledgment is due to T. Koenig for measuring the electron spin density and S. R. Faris for measuring the resistivity and also to J. L. Fitch, R. F. Burdyn, and C. S. Kuhn for their continued interest in the problem.

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Synopsis

Similar infrared spectra are observed when cyclopentadiene is polymerized with any of the following catalysts: stannic chloride, titanium tetrachloride, or the combination of titanium tetrachloride and aluminum alkyl. When the resulting polymer is brominated, it spontaneously undergoes a spectacular dehydrobromination which gives a series of color changes and finally a black carbonlike material that is insoluble in common laboratory solvents. Consideration of the remaining bromine content of the dehydrobrominated polymer along with the visual spectrum produced by the actively dehydrobrominating polymer, the infrared and ultraviolet spectra and the visual spectrum of the original and isomerized polycyclopentadiene indicate the structure of the polymer and the mode of polymerization. The bromodehydropolycyclopentadiene shows unusual physical properties; it has a resistivity of 10^6 ohm-cm. and an electron spin density of 10^{18} spins/g. The polymer also exhibits unusual thermal stability. In a nitrogen atmosphere at 900°C. it is still 50% intact and is not completely pyrolyzed until a temperature of 1100°C. is reached.

Résumé

On a observé des spectres infra-rouges similaires lorsque le cyclopentadiène est polymérisé avec un des catalyseurs suivants: le chlorure stannique, le tétrachlorure de titane, ou un mélange de tétrachlorure de titane avec un alcoyl-aluminium. Pendant la bromation du polymère formé, celui-ci subit une déshydrobromation spontanée qui provoque une série de changements de couleur, et finalement donne lieu à un polymère semblable à du noir de carbone, insoluble dans les solvants de laboratoire usuels. On peut trouver la structure du polymère, et la façon de polymériser, lorsqu'on considère la teneur en brome du polymère déshydrobromé ainsi que le spectre visible du polymère pendant la déshydrobromation et les spectres infra-rouges, visible et ultra-violet du polycyclopentadiène original et isomérisé. Le bromodéshydropolycyclopentadiène possède des propriétés physiques singulières. La résistivité est de 10^6 ohm-cm; la densité des spins électroniques est de 10^{18} spins par gramme. La stabilité thermique des polymères est aussi remarquable: à 900°C, sous atmosphère d'azote, le polymère reste intact pour 50% et ne peut être complètement pyrolysé que quand la température est de 1.100°C.

Zusammenfassung

Polymere mit ähnlichen Infrarotspektren werden bei der Polymerisation von Cyclopentadien mit einem der folgenden Katalysatoren erhalten: Zinn-IV-chlorid, Titantetrachlorid oder eine Titantetrachlorid-Aluminium-alkyl-Kombination. Bei der Bromierung ergibt das Polymere eine auffällige, spontane Bromwasserstoffabspaltung mit einer Reihe von Farbänderungen und schliesslicher Bildung eines schwarzen,

kohleartigen Stoffes, der in den üblichen Lösungsmitteln unlöslich ist. Der verbleibende Bromgehalt des dehydrobromierten Polymeren sowie das während der Bromwasserstoffabspaltung des Polymeren im Sichtbaren auftretende Spektrum, das Infrarot- und Ultraviolettspektrum und das Spektrum im Sichtbaren des ursprünglichen und des isomerisierten Polycyclopentadiens geben Hinweise auf die Struktur des Polymeren und die Art der Polymerisation. Das Brom-dehydropolycyclopentadien zeigt ungewöhnliche physikalische Eigenschaften; es besitz einen spezifischen Widerstand von 10^6 Ohm × cm und eine Elektronenspindichte von 10^{18} Spins pro Gramm. Das Polymere zeigt auch eine ungewöhnliche thermische Stabilität. In einer Stickstoffatmosphäre ist es bei 900°C noch zu 50% intakt und erleidet erst bei einer Temperatur von 1100°C vollständige Pyrolyse.

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Polymères à Longues Séquences de Doubles Liaisons Conjuguées: Préparation et Propriétés

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Le vif intérêt qui s'est manifesté ces dernières années pour les polymères semi-conducteurs est à l'origine des nombreux travaux effectués en vue d'obtenir des substances macromoléculaires possédant des électrons mobiles. C'est ainsi qu'ont été préparés des polyparaaminoquinones,[1] des polyacrylonitriles thermiquement polycyclisés,[2] et bien d'autres. Parmi tous ces produits, les polymères à doubles liaisons conjuguées présentent l'avantage de la simplicité du modèle moléculaire, et c'est pourquoi nous nous sommes attachés à leur étude.

Pour préparer de tels polymères, on peut utiliser diverses voies: (*1*) la polymérisation de l'acétylène[3] ou de ses dérivés, comme le phénylacétylène,[4] et la polycrotonisation de l'aldéhyde acétique ou de l'aldéhyde crotonique[5] ne progressent guère au-delà de la formation d'oligomères fortement colorés et peu solubles: (*2*) au lieu d'édifier la chaîne insaturée par polymérisation. on peut chercher à créer sur une chaîne macromoléculaire saturée des séquences de doubles liaisons conjuguées. Pour ce faire, on peut partir d'alcool polyvinylique ou d'acétate de polyvinyle,[6] mais nous avons choisi des halogénures de polyvinyle qui se prêtent volontiers à une réaction d'élimination d'hydracide.

Il importe de remarquer que les polymères ainsi obtenus sont des copolymères séquencés constitués de séquences du polymère initial et de séquences de doubles liaisons conjuguées.

En vue d'une étude du comportement chimique, optique, électrique et magnétique de telles chaînes macromoléculaires, nous avons étudié la déhydrohalogénation des chlorures et bromures de polyvinyle et avons en particulier tenté d'obtenir des séquences de doubles liaisons conjuguées aussi longues que possible.

I. CRÉATION DE DOUBLES LIAISONS CONJUGUÉES SUR LA CHAÎNE DE CHLORURE DE POLYVINYLE (PVC)

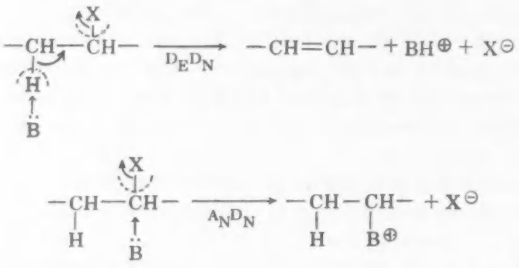
Le chlorure de polyvinyle est sensible à l'action des radiations électromagnétiques, de la chaleur et des agents basiques. Il libère ainsi de l'acide chlorhydrique et se colore. De nombreux auteurs se sont attachés à élucider le mécanisme de ces déhydrohalogénations, afin d'en déduire des procédés de stabilisation du PVC.

Notre étude se situe dans une optique opposée. Nous avons cherché à réaliser une déhydrohalogénation poussée du PVC afin d'obtenir des produits nouveaux, largement insaturés et bien définis. Peu de travaux ont été, jusqu'ici, effectués dans la même perspective. Citons cependant Bohrer[7] qui a étudié l'action de la morpholine sur le chlorure de polyvinylidène, Oster, Oster, et Kryszewski[8] qui ont soumis le PVC au rayonnement ultraviolet; l'action de la chaleur sur le chlorure de polyvinylidène[9] et sur le polyacrylonitrile[2] ont fait l'objet de travaux prometteurs.

Mécanismes de Déhydrohalogénation

La déhydrohalogénation thermique[10] procède, selon Winkler,[11] d'un mécanisme radicalaire. L'activation allylique facilite la création des doubles liaisons conjuguées, mais les réactions entre sites éloignés d'une même chaîne, ou entre radicaux portés par des chaînes différentes ne sont pas exclues. Il peut donc y avoir des cyclisations et des pontages, qui sont des réactions parasites.

L'action des bases sur le PVC relève, en revanche, d'un mécanisme ionique. On sait que l'action d'une base sur un dérivé halogéné conduit soit à une élimination d'hydracide, ce qui est la réaction attendue, soit à une réaction de substitution de l'halogène. Ces deux réactions ont lieu concurremment dans la plupart des cas. En utilisant les schémas réactionnels et les notations d'Ingold,[12] on peut représenter ainsi ces deux types d'attaque:



Les deux réactions peuvent avoir lieu selon des mécanismes bimoléculaires ou unimoléculaires. Nous ne nous préoccuperons pas ici de savoir quel mécanisme l'emporte sur l'autre: en effet, ce qui nous importe est de favoriser l'élimination par rapport à la substitution, qui est ici une réaction parasite interrompant la conjugaison.

Parmi les facteurs susceptibles d'agir sur l'orientation de la réaction, nous citerons: (*1*) la force de la base qui conditionne son affinité pour le proton, (*2*) la polarité du solvant qui, accélérant les deux réactions, ne peut favoriser l'une par rapport à l'autre, (*3*) la nature de l'halogène: l'énergie de la liaison C—Br étant inférieure à celle de la liaison de C—Cl, on peut s'attendre à ce que le bromure de polyvinyle soit plus sensible à l'action des bases que ne l'est le PVC.

Déhydrohalogénation du PVC par les Bases

Le traitement du PVC par les bases conduit toujours à des produits fortement colorés et peu solubles. Que la base soit un hydroxyde[13] un alcoolate,[14] une amine ou une base azotée hétérocyclique[7,13a,15] la substitution et la réaction d'élimination se déroulent toujours de façon concomitante. Dans le cas des bases azotées, en particulier, la teneur notable du produit en azote atteste de l'importance de la substitutution parasite.

Par contre, rien ne permet de supposer que des cyclisations ou des pontages, aient lieu si on prend soin d'opérer à des températures telles que la déhydrohalogénation thermique puisse être tenue pour négligeable. Cette condition n'a pas toujours été respectée dans les travaux antérieurs au nôtre. Aussi avons-nous repris les recherches dans ce domaine, en opérant systématiquement à 80°C. Les résultats de cette étude seront publiés ultérieurement; mais nous indiquerons dès à présent que les bases faibles ne donnent lieu qu'à une faible déhydrohalogénation, alors que dans le cas des bases fortes la réaction d'élimination est toujours accompagnée de la substitution de l'halogène par la base.

Nous avons également étudié l'action de bases particulières, les carbanions des composés organométalliques.[16] Ces bases ont un comportement analogue à celui des bases organiques classiques.

Pour obtenir des chaînes macromoléculaires portant des longues séquences de doubles liaisons conjuguées, sans qu'il y ait de cyclisation, ni de pontages, ni de réactions parasites de substitution, nous nous sommes alors tournés vers d'autres systèmes basiques plus complexes, les sels métalliques dissous dans le diméthylformamide (DMF).

II. DEHYDROHALOGENATION PAR LES SYSTÉMES SEL MÉTALLIQUE–DIMÉTHYLFORMAMIDE

Signalé en premier lieu par Holysz,[17] le système ClLi–DMF s'est révélé très actif comme agent de déhydrohalogénation du PVC et du PVBr.[18]

Le DMF est lui-même une base très faible: les résultats d'une action prolongée de ce solvant sur le PVC à 80°C sont très modestes; aussi le rôle du DMF est-il plutôt ici celui d'un solvant très polaire. Il dissout de nombreux sels minéraux, et nous avons constaté qu'il donne avec le ClLi des composés d'addition bien cristallisés.

Ce sont les résultats de l'action sur le PVC et le PVBr de plusieurs systèmes (sel métallique–DMF) que nous allons exposer et discuter dans ce qui suit.

Partie Expérimentale

Produits Utilisés

Polymères. Le PVC nous a été aimablement fourni par la Cie St. Gobain. Il a été purifié par précipitation dans le méthanol d'une solution dans le tétrahydrofuranne. Sa teneur en chlore était de 56,73% (théorique:

56,80%) et sa masse moléculaire, déterminée par diffusion de la lumière, de 72.000.

Le PVBr a été préparé au laboratoire, par polymérisation du bromure de vinyle en masse, à température ambiante, par irradiation ultra-violette. Le polymère obtenu a été dissous dans le THF et précipité par le méthanol. Sa masse moléculaire est de 69.000 et sa teneur en brome de 74,65% (théorique: 74,77%). Il a été conservé à l'obscurité et au frais.

Solvants. Les solvants utilisés dans cette étude, tétrahydrofuranne, diméthylformamide et cyclohexanone ont été purifiés et distillés par les méthodes classiques. Il a été vérifié qu'ils ne contenaient pas de peroxydes et que leur teneur en eau était inférieure à 20 mg/l.

Sels Métalliques. Nous avons employé des sels Merck purs et anhydres. Avant utilisation, ils ont été chauffés sous vide. Dans le cas du chlorure de magnésium, cependant, la déshydratation de l'hydrate commercial $MgCl_2 \cdot 6H_2O$ doit être effectuée par chauffage dans un courant de gaz chlorhydrique.

Procédure Expérimentale

Appareillage Utilisé. Nous avons effectué l'ensemble des opérations de mise en solution du PVC, de traitement par le système (sel métallique–DMF), de précipitation, de filtration et de séchage dans un appareil

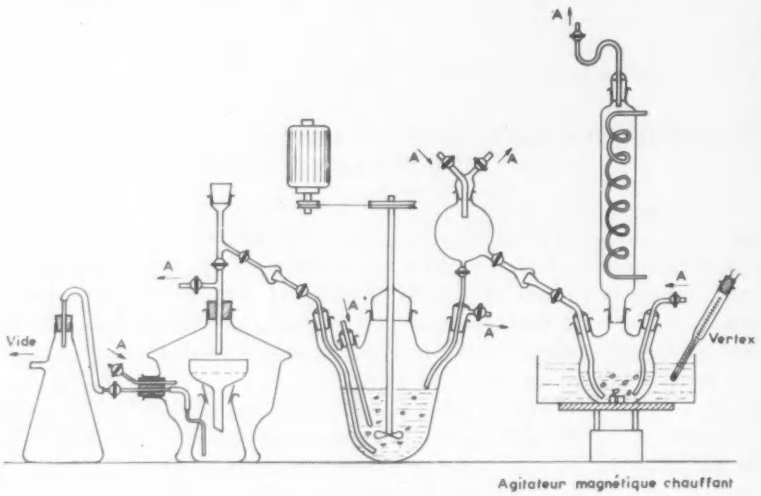


Fig. 1. Appareillage utilisé.

étanche, sous atmosphère d'argon (Fig. 1). La réalisation de cette installation s'est avérée nécessaire en raison de la sensibilité des produits déhydrohalogénés à l'oxygène atmosphérique.

Conditions Expérimentales. La majorité de nos expériences a été effectuée sur le PVC. La concentration du polymère est de 10 g/l (0,16 unités monomère/l). Le rapport de la concentration molaire du sel à la concentration en unités monomères est indiquée par le rapport K que nous avons fait varier de 0,5 à 6,25: la concentration du sel allait donc de 0,08 à 1 mol/l. La plupart des expériences ont été conduites à 80°C pendant 8 h. Les expériences effectuées sur le PVBr ont été conduites à température ambiante et leur durée était en général de plusieurs jours.

Caractérisation des Produits Obtenus

En raison de leur insolubilité quasi-totale dans tous les solvants et de leur très forte coloration il n'a pas été possible d'envisager de caractériser les polymères déhydrochlorurés à l'aide des techniques physicochimiques classiques: diffusion de la lumière, viscosité, sédimentation etc. En revanche nous avons effectué sur nos produits des dosages de chlore résiduel, pour en caractériser le taux d'insaturation, et des mesures spectroscopiques ultra-violette et visible.

Les analyses de chlore ont été faites par la méthode microgravimétrique de Pregl après minéralisation selon Carius.

Les spectres ultra-violets et visibles des solutions (ou suspensions) de nos polymères en cours de déhydrohalogénation ont été pris soit à l'aide d'un spectrophotomètre enregistreur Lerès T2D, soit à l'aide d'un spectrophotomètre Zeiss PMQ II.

Résultats Expérimentaux

Il apparaît que, selon les conditions expérimentales, la réaction de déhydrohalogénation présente deux allures différentes qui sont mises en évidence par les spectres ultra-violet et visible.

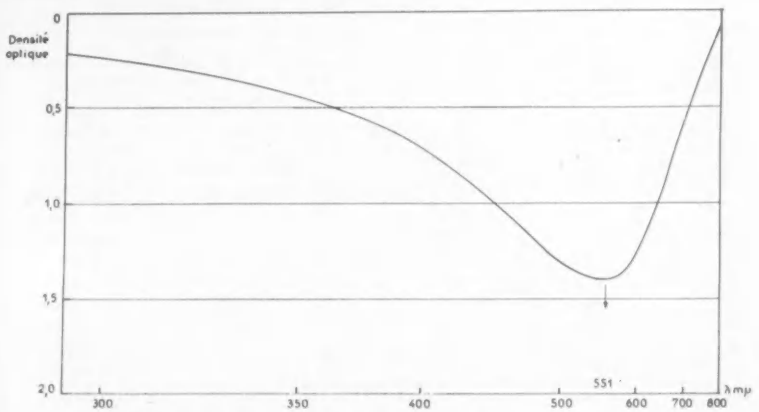


Fig. 2. Spectre d'absorption caractéristique du processus "violet."

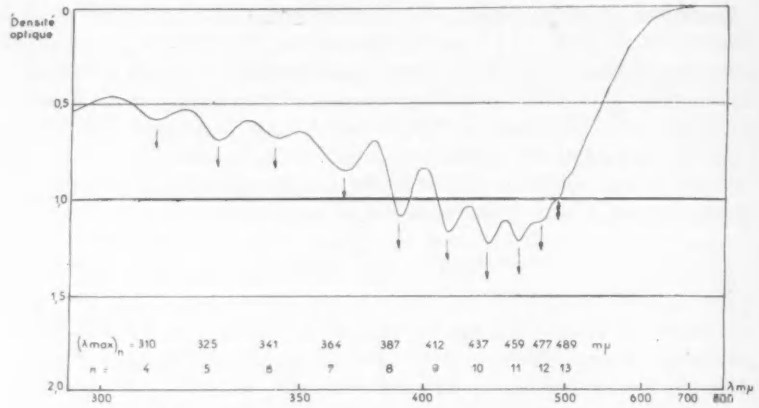


Fig. 3. Spectre d'absorption caractéristique du processus "rouge."

Dans un premier cas la solution prend une teinte rose-violette, puis violette, qui va en s'approfondissant au cours du temps. La courbe d'absorption spectrale est caractérisée par un maximum unique qui se situe en général vers 550 mμ (Fig. 2). Ce processus, que nous qualifions de "violet," se rencontre en particulier quand la réaction est conduite en milieu DMF pur.

Dans d'autres cas la solution devient tout d'abord jaune, puis orange, puis rouge et finalement brun foncé. Nous avons qualifié de "rouge" ce deuxième processus. Les spectres d'absorption des solutions sont caractérisés ici par une série de maxima d'absorption (Fig. 3).

L'ensemble des résultats de nos expériences déhydrohalogénation des halogénures de polyvinyle, par divers sels, dans différents milieux solvants, sont portés au Tableau I. Des résultats quantitatifs sont portés au Tableau

TABLEAU I

Polymère	Solvant[a]	Type "violet"	Type "rouge"	Aucune déhydro-halogénation
PVC (80°C)	DMF	ClLi Cl_2Mg anhydre	BrLi, acétates Cl_2Mg, $6H_2O$	Cl_2Ni, Cl_2Co Cl_2Cu, Cl_2Zn ClNa, ClK NO_3Li, CO_3Li_2 ClH
"	DMF/THF	ClLi	—	ClH
"	DMF/A	—	ClLi	—
"	DMF/B	ClLi	—	—
PVBr (20°C)	DMF	ClLi, BrLi, ClH	—	—
"	DMF/THF	ClLi, BrLi, ClH	—	—

[a] A = cyclohexanone, acétylacétone; B = dioxane, méthy éthyl cétone, acétophénone, benzophénone, anisole.

II; les paramètres de l'étude sont les suivants: Solvant = rapport du volume de DMF au volume de THF dans le mélange solvant; K = rapport du nombre de moles de sel au nombre total d'unités monomère en solution; t = durée de l'expérience en heures; % Cl = valeurs corrigées pour tenir compte du DMF retenu ou fixé par la chaîne macromoléculaire; % DL =

TABLEAU II

Solvant	K	t, h	Température, °C	% Cl	% DL	No.
DMF pur	6,25	8	80	38,92	52,50	195
	6,25	29	90	18,20	83,61	61
	2,08	8	80	48,79	28,75	200
	2,08	8	90	43,18	43,15	196
	2,08	8	110	26,04	73,97	177
	2,08	24	80	47,33	32,53	171
	1,25	8	80	53,61	12,05	201
	0,5	8	80	55,59	5,06	150
DMF/THF, 1/1	6,25	8	80	48,87	28,11	54
	2	8	80	55,13	6,85	202
DMF/THF, 3/1	6,25	8	80	47,83	31,12	169
	2	8	85	50,35	23,59	199

taux de déhydrochloruration du polymère initial, c'est-à-dire nombre de motifs monomères ayant subi la réaction d'élimination par rapport au nombre total de motifs. Les résultats de l'étude spectroscopique que nous avons effectuée sur les produits "rouges" en solution diluée sont portés au

TABLEAU III

			Nos produits, $(\lambda_{max})_n$ mμ		
n	Diméthy-polyènes, $(\lambda_{max})_n$, mμ[a]	Poly-acétylènes, $(\lambda_{max})_n$, mμ[b]	Gamme	Valeur la plus fréquente observée	$k \times 10^{-4}$
4	299	—	305–312	312	2,43
5	326	330	324–327	325	2,11
6	352	360	340–346	342	1,95
7	—	370	364–368	365	1,90
8	395,5	395	386–391	387	1,87
9	412,5	—	412–416	413	1,90
10	432[c]	420	436–442	437	1,91
11	—	450	456–463	460	1,92
12	—	—	477–479	477	1,90
13	—	475	482–492	490	1,85
14	—	—	499	499	1,78

[a] Résultats de Bohlmann et Mannhardt.[19]

[b] Résultats de Natta.[3]

[c] Valeur obtenue pour C_6H_{13}—(CH=CH)$_{10}$—C_6H_{13}.

Tableau III. En regard des valeurs de λ_{max} que nous avons observées, nous avons fait figurer les valeurs des λ_{max} observées par Bohlmann et Mannhardt[19] sur une série de diméthylpolyènes de synthèse. Par comparaison avec ces valeurs, on peut attribuer chacun des maxima observés à l'absorption de séquences de n doubles liaisons conjuguées. D'autre part, Lewis et Calvin[20] ayant établi que la variation de $(\lambda_{max})_n$ avec n est de la forme

$$(\lambda_{max})_n^2 = kn$$

nous avons calculé la valeur de k pour les différents maxima présentés par nos produits (Tableau 3). La loi de Lewis et Calvin semble constituer une approximation valable pour des valeurs de n allant de 5 à 14.

D'autre part, quand n croît, les $(\lambda_{max})_n$ ont des valeurs de plus en plus voisines et, selon certains auteurs,[21] elles tendraient rapidement vers une limite. D'autre part, la dispersion du prisme du spectrophotomètre étant plus faible pour les grandes longueurs d'onde, l'échelle du spectrographe Lérès est en $1/\lambda^2$. Pour ces deux raisons, les maxima d'absorption relatifs à des séquences insaturées longues ne peuvent plus être distingués et l'absorption de ces séquences se traduit, sur les spectres, par une bande d'absorption unique et large.

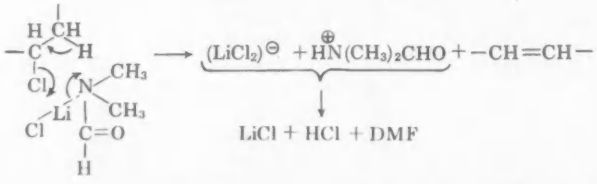
Il résulte donc de cette étude que les produits "rouges" contiennent de nombreuses séquences insaturées, relativement courtes, identifiables du point de vue de leur longueur, alors que, dans le cas des produits "violets" au contraire, la déhydrohalogénation conduit essentiellement à des longues séquences de doubles liaisons, dont on ne peut toutefois préciser la longueur.

Discussion des Résultats Expérimentaux

Mécanisme de la Déhydrohalogénation par le Système ClLi/DMF

Les réactions de déhydrohalogénation que nous avons étudiées résultent, nous l'avons vu, de l'action d'un sel métallique (le plus souvent ClLi) sur l'halogénure de polyvinyle en solution dans le DMF.

L'élimination d'HCl résulterait, selon Holysz[17] d'un déplacement électronique concerté englobant, en un cycle à 6 chaînons, le composé halogéné, la molécule de DMF et la molécule de sel:



Ce mécanisme rend compte d'une partie des faits expérimentaux. Il ne nous paraît cependant pas entièrement satisfaisant, pour plusieurs raisons.

(*1*) En donnant le rôle le plus important au pouvoir coordinant du cation, l'hypothèse d'Holysz ne peut expliquer pourquoi certains sels sont actifs et d'autres non.

(*2*) On peut chercher à rattacher la déhydrochloruration aux réactions connues d'élimination; c'est alors à l'anion qu'il faut attribuer le rôle essentiel, car il est susceptible de se comporter comme une base. Il faut donc tenir compte de la dissociation du sel et de la solvatation des ions.

(*3*) En faisant intervenir directement le DMF, par le doublet libre de son atome d'azote, Holysz l'assimile à une base. Or, le formamide, de basicité comparable, est inefficace. Quant au DMF, en absence de sel, il se comporte comme une base très faible. Il nous semble donc qu'il faille limiter le rôle du DMF à celui d'un solvant à la fois polaire et aprotique.

De récentes recherches sur ces milieux[22] ont montré que les anions y sont d'autant moins solvatés que leur diamètre est plus petit. Ils peuvent donc y jouer le rôle de base qu'en raison de leur solvatation ils ne peuvent remplir en milieu aqueux. On peut donc supposer qu'en milieu DMF l'agent de la déhydrochloruration n'est autre que l'anion Cl^-. Les sels des métaux lourds, bien que solubles dans le DMF n'y sont pas dissociés:[23] ainsi peut-on expliquer que les chlorures de nickel et de cobalt soient totalement inactifs.

L'anion Cl^- jouant le rôle de base dans la réaction d'élimination, peut également donner lieu à des réactions de substitution qui, bien entendu, passent inaperçues si le polymère est le PVC. Elles sont par contre aisément décelables quand on fait agir LiCl sur du PVBr, ou LiBr sur du PVC.

Si nous envisageons maintenant le cas où la réaction de substitution présente un caractère d'irréversibilité, la longueur des séquences déhydrochlorurables est alors limitée par la présence de ces substituants. C'est le cas quand la réaction d'élimination est due à l'action du système acétate de lithium–DMF. Le processus est "rouge," les séquences polyéniques sont courtes et la présence sur la chaîne de groupes acétate est mise en évidence par spectrographie infra-rouge.

Ces résultats nous incitent à penser que la déhydrohalogénation des halogénures de polyvinyle sous l'action des systèmes sels métalliques–DMF est normalement de type "violet" et conduit à de très longues séquences polyéniques. Le processus "rouge" de déhydrochloruration n'apparaît que quand la longueur des séquences déhydrochlorurables est limitée par des substituants de la chaîne qui ne peuvent participer à la réaction d'élimination.

De nombreux faits expérimentaux étayent ces deux hypothèses relatives au mécanisme de l'élimination. Nous en citerons quelques-uns à titre d'example.

(*1*) La déhydrobromuration du PVBr, à température ambiante, par HCl en solution DMF s'est avérée possible, alors que le même essai, effectué à 80°C sur le PVC n'a donné aucun résultat. L'ion Li^+ est mieux solvaté par le DMF que l'ion H^+: la concentration des ions Cl^- est donc plus grande dans le cas du ClLi que dans le cas de HCl. Comme pour le PBBr

l'arrachement du proton par Cl^- est facilité par la labilité de la liaison C—Br, on comprend que les ions Cl^- ne soient actifs que vis-à-vis de ce polymère.

(*2*) Quand on traite, à 80°C, du PVC par LiBr, la réaction de substitution du Br au Cl tend à créer des liaisons C—Br sur la chaîne. A cette température ces liaisons sont très fragiles, et un grand nombre de sites initiateurs sont ainsi créés sur la chaîne. La limitation mutuelle des séquences de doubles liaisons conjuguées conduit alors au processus "rouge." Dans le cas inverse, PVBr traité à température ambiante par LiCl, la déhydrochloruration est de type "violet" car la réaction d'élimination l'emporte largement sur la réaction de substitution du brome par le chlore.

(*3*) Nous avons effectué la déhydrochloruration d'échantillons de PVC dont une proportion connue d'atomes de chlore avait été substituée par des groupes diphénylméthyle. Ces substituants ne pouvant participer à la réaction de déhydrochloruration, celle-ci est, comme on doit s'y attendre, de type "rouge."[24]

(*4*) La présence, dans le milieu réactionnel, de cyclohexanone ou d'acétylacétone conduit à des substitutions parasites irréversibles décelées par spectrographie infra-rouge (groupes carbonyles) et entraîne l'apparition du processus "rouge." Cela n'est pas dû à la diminution de la polarité du milieu réactionnel car la présence de solvants peu polaires, dioxanne ou tétrahydrofuranne, si elle modifie la cinétique de la réaction, n'en change pas le mécanisme; la réaction d'élimination reste dans ces deux derniers cas de type "violet."

(*5*) La même remarque est valable si le sel utilisé est le chlorure de magnésium. Le sel hydraté commercial, $MgCl_2$, $6H_2O$, conduit au processus "rouge," alors que la déhydrohalogénation est de type "violet" si l'on emploie $MgCl_2$ parfaitement déshydraté. La substitution parasite est ici celle de groupes OH qui remplacent irréversiblement certains atomes de chlore.

Etude Quantitative de l'Efficacité du Système ClLi–DMF

L'étude que nous avons entreprise ne prétend nullement établir la cinétique de la déhydrochloruration par ClLi–DMF. Nous nous sommes surtout attachés à voir jusqu'où on pouvait pousser la déhydrochloruration, et quelles étaient les conditions expérimentales les plus appropriées à l'obtention de produits fortement insaturés.

Le Tableau 2 appelle les commentaires suivants.

Influence de la Concentration en Sel. Plus le rapport K est élevé, plus rapidement progresse la déhydrochloruration. Dans des conditions par ailleurs identiques, on passe de 52,50% de DL pour $K = 6{,}25$ (n° 195) à % DL = 28,75 pour $K = 2$ (n° 200), % DL = 12,05 pour $K = 1{,}25$ (n° 201), % DL = 5,06 pour $K = 0{,}5$ (n° 150).

Influence de la Température. Plus celle-ci est élevée, plus le taux d'insaturation augmente. Ainsi on passe de % DL = 28,75 à 80°C (n° 200)

à % DL = 43,15 à 90°C (n° 196) et à % DL = 73,97 à 110°C (n° 177).

Influence de la Durée de l'Expérience. Au cours du temps, le dégré de déhydrochloruration augmente. Pour le polymère n° 200, on a % DL = 28,75 au bout de 8h, et % DL = 32,53 au bout de 24 heures (n° 171).

Influence de la Polarité du Solvant. Le tableau montre très nettement que plus le milieu est polarie, plus vite on atteint un taux d'insaturation élevé. Si l'on compare les produits n° 195, 169 et 54, préparés dans des conditions identiques, mais dans le DMF pur, le mélange DMF/TMF 3/1 et le mélange DMF/THF 1/1, on voit qu'on passe de % DL = 52,50 (n° 195) à % DL = 31,12 (n° 169) puis à % DL = 28,11 (n° 54).

On a donc intérêt à travailler avec une concentration en sel élevée, et en milieu DMF pur. Bien que l'élévation de la température favorise la réaction, on se rappellera qu'elle risque d'entraîner des réactions de pontage d'origine thermique.

Caractéristiques des PVC Déhydrohalogénés par ClLi

Les produits déhydrohalogénés contiennent fréquemment de faibles teneurs, équimoléculaires, d'oxygène et d'azote. Il y a donc du DMF retenu à l'intérieur du produit. Il ne peut guère s'agir de DMF "quaternisé"—ce qui conduirait à un produit trop instable—mais plutôt de DMF retenu mécaniquement.

D'autre part, du chlorure de lithium ou de l'acide chlorhydrique peuvent également se trouver retenus dans les granules de polymère précipité, en quantités assez importantes pour que les résultats des dosages en soient affectés. Il convient d'éviter que la précipitation du produit ne soit trop brutale, afin que la quantité de ces impuretés restant fixées sur les grains de polymère soit réduite au minimum. Pour tenter d'éliminer le sel, avant la précipitation du polymère, nous avons filtré certaines solutions-mères sur des gels de dextrane réticulé (Sephadex, fabriqué par Pharmacia, Uppsala, Suède). Les résultats ont été encourageants mais ce procédé de filtration est très lent.

Lorsque la réaction d'élimination affecte 30 à 40% des unités monomères, le produit devient insoluble. Nous ne pensons pas qu'il faille attribuer ce phénomène à la formation de pontages intermoléculaires—improbables ici—mais simplement à la prédominance des séquences polyéniques en structure "trans," rigides et non solvatées, par rapport aux séquences PVC solubles qui sont maintenues écartées par les parties déhydrohalogénées. D'autre part, les solutions elles-mêmes ont tendance à floculer quand on arrête l'agitation, et cette floculation apparaît irréversible, même en l'absence d'air ou de tout réactif susceptible de provoquer des pontages. On pourrait peut-être expliquer ce phénomène par des couplages entre orbitales π de séquences de molécules différentes, rendus possibles en l'absence d'agitation; une fois établis, ces couplages ne se défont que difficilement.

Quelles que soient les difficultés rencontrées au cours de la préparation et de la purification de nos produits, il reste que, pour la première fois, il a

été possible de préparer des polymères à longues séquences polyéniques dans des conditions expérimentales telles que les réactions parasites de cyclisation, de pontage et de substitution puissent raisonnablement être tenues pour négligeables.

III. ETUDE DES PROPRIÉTÉS ÉLECTRIQUES DES PVC DÉHYDROCHLORURÉS

La position du maximum d'absorption dans le visible des produits déhydrohalogénés montre que les électrons π sont fortement délocalisés le long du squelette carboné. Pour savoir si ces électrons délocalisés peuvent passer d'une séquence à une autre et d'une molécule à une autre, nous avons entrepris des mesures de conductivité électrique. La valeur absolue de la conductivité, ainsi que sa variation en fonction de la température, peuvent, en effet, nous apporter des informations sur la mobilité des électrons dans les échantillons de nos produits et sur les couplages des orbitales π des séquences polyéniques.

Les produits que nous avons préparés sont insolubles, et donc impropres à la fabrication de films. Les mesures de conductivité ont donc dû être effectuées sur des poudres comprimées en pastilles. Ces mesures sont délicates car les causes d'erreurs liées à l'hétérogénéité de la substance sont non seulement nombreuses, mais encore difficiles à évaluer.

Quand on soumet l'échantillon—considéré comme un agglomérat compact de grains de polymère—à une tension alternative, il faut, à côté de la résistance et de la capacité propres de l'échantillon, R_e et C_e, tenir compte des résistances et capacités des contact entre grains, R_c et C_c. Huggins[25] a récemment traité ce problème: il a calculé, en fonction de la fréquence ω, de R_e, R_c, C_e et C_c, la résistance parallèle équivalente, R_p, et la capacité parallèle équivalente C_p, qui sont les grandeurs effectivement mesurées. Lorsque la fréquence est très faible, R_p tend vers $R_c + R_e$, et C_p vers C_c. Au contraire, quand la fréquence devient grande, R_p a pour valeur R_e, et C_p, C_e. Les mesures en courant continu ne semblent donc pas être appropriées à l'étude d'échantillons constitués de grains de polymère agglomérés.

Eley[26] a mesuré la valeur de la résistance parallèle équivalente d'un échantillon constitué par une poudre de cristaux d'isodibenzanthrone. Il a montré que lorsque la fréquence augment, R_p tend vers une valeur limite qu'il considère comme la résistance propre de l'échantillon. Cette valeur n'est atteinte que lorsque ω est égal à 5 Mc/s. La pastille sur laquelle il a effectué ces mesures était obtenue sous une pression de 80 kg/cm^2. On peut raisonnablement penser que si la poudre à étudier est soumise à une plus forte pression, 10 tonnes/cm^2 dans notre cas, les contacts entre grains seront meilleurs, et la valeur limite de la résistance parallèle équivalente sera atteinte pour des fréquences plus basses. Il est évident que, dans ces conditions, il serait important de mesurer la conductivité dans une gamme étendue de fréquences. Cependant, à 1592 c/s, fréquence à laquelle nous pouvions facilement opérer, les résistances sont déjà 1000 fois plus faibles

qu'à fréquence nulle: nous avons donc admis qu'en première approximation cette fréquence était située au delà de la bande d'absorption liée à l'existence d'hétérogénéités.

Partie Expérimentale

Les produits ont été comprimés en pastilles dans une presse à pastiller Kopff[27] sous une pression d'environ 10 tonnes/cm². Les échantillons ont un diamètre de 1,2 cm (s = 1,13 cm²) et leur épaisseur est comprise entre 0,1 et 0,5 mm. Pour que soient assurés de bons contacts entre la surface de l'échantillon et celle des électrodes, les deux faces de la pastille ont été argentées par métallisation sous vide. Signalons toutefois que, dans le cas des polymères fortement insaturés, qui sont constitués de petits grains très durs, il ne nous a pas été possible de faire des pastilles suffisamment homogènes. Nous avons donc dû renoncer à effectuer des mesures sur ces échantillons.

La cellule employée est représentée sur la Figure 4. Les deux électrodes (a, b) sont isolés du corps de la cellule (c) par du téflon (d). L'une des

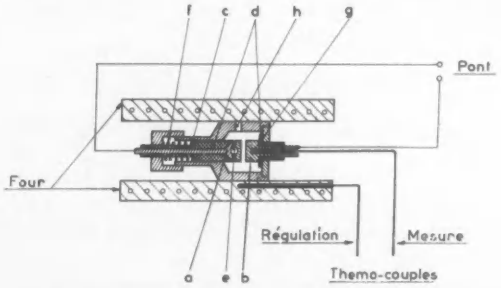


Fig. 4. Cellule de mesure de la conductivité.

électrodes peut pivoter autour d'une petite bille (e) et l'échantillon est fortement pressé entre les deux électrodes au moyen d'un ressort (f). A l'intérieur d'une des deux électrodes, à un demi-millimètre de sa surface, se trouve logée la soudure chaude d'un thermocouple qui sert à mesurer la température de l'échantillon (g).

Le corps de la cellule est percé de trous (h) permetant l'évacuation de l'air que si trouve à l'intérieur de la cellule, ce qui permet un dégazage continu de la pastille.

La cellule est placée à l'intérieur d'un four chauffé électriquement dont la température, mesurée par un thermocouple, est maintenue à la valeur choisie par un régulateur de température Pyrectron.

La cellule et le four sont placés dans une enceinte évacuée à 10^{-6} mm Hg par un groupe de pompage Edwards ISC50B/F203

Les mesures de conductivité et de capacité sont effectuées au moyen diun pont Wayne-Kerr B 221 travaillant à la fréquence fixe de 1592 c/s.

Dans les conditions où nous avons opéré, la tension aux bornes de la cellule était de l'ordre de 3 V.

Résultats Expérimentaux

Si l'on porte le logarithme de la conductivité mesurée σ en fonction de l'inverse de la température absolue, on obtient, dans tous les cas étudiés,

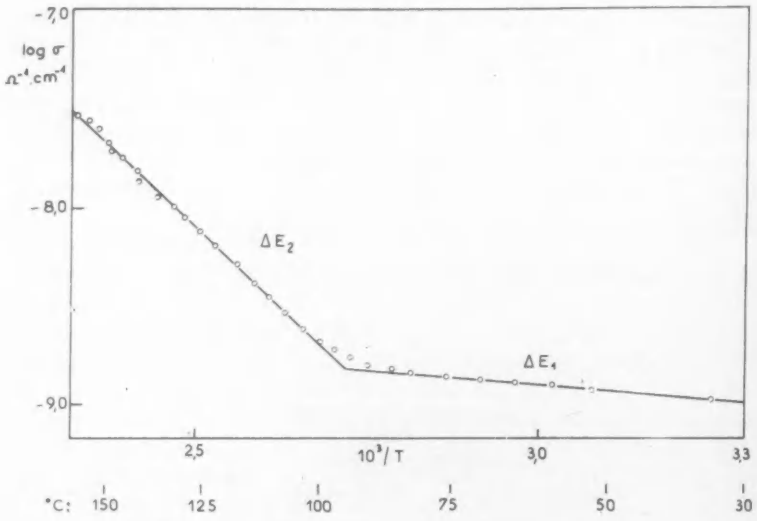


Fig. 5. Variation reproductible de la conductivité en fonction de $10^3/T$.

une courbe expérimentale du type de celle représentée sur la Figure 5. Cette courbe n'est en général obtenue qu'après deux cycles de chauffage et de refroidissement, pendant lesquels le comportement de σ est très différent

TABLEAU IV

Echantillon	Exp. n°	% DL[a]	ρ (25°C), ohm-cm $\times 10^{-10}$	ΔE_2, eV	ΔE_1, eV	T_c, °C
177	17	74	2	0,70	~0	97
177[b]	16	74	2	0,69	0,12	82
189	14	43	3	0,87	0,21	95
205	26	38	2,6	1,24	~0	91,5
178	22	32	2,9	1,30	~0	103
197	25	32	1,7	1,26	~0	104
172	10	6	1,23	2,41	0,14	80
172[c]	11	6	1,1	2,79	~0	98,5

[a] % DL = pourcentage de doubles liaisons conjuguées.
[b] Avec 10% ClLi.
[c] Après séjour de 3h à 180°C.

(Fig. 6). Ce n'est qu'à partir du troisième chauffage que la courbe log σ en fonction de $1/T$ a un comportement reproductible. Les points expérimentaux se placent alors sensiblement sur deux droites. Si l'on admet, pour la variation de σ, la loi

$$\sigma = \sigma_0 \exp \{-E/2kT\}$$

on peut définir deux énergies d'activation différentes, l'une ΔE_1 dans le domaine des températures peu élevées, l'autre ΔE_2 pour les températures plus élevées. ΔE_2 est toujours sensiblement supérieur à ΔE_1, qui est général très petit, et peut être nul ou faiblement négatif. Les deux droites de pente ΔE_2 et ΔE_1 se coupent en un point que nous appellerons "point de transition," et dont l'abscisse définira une "température critique" T_c.

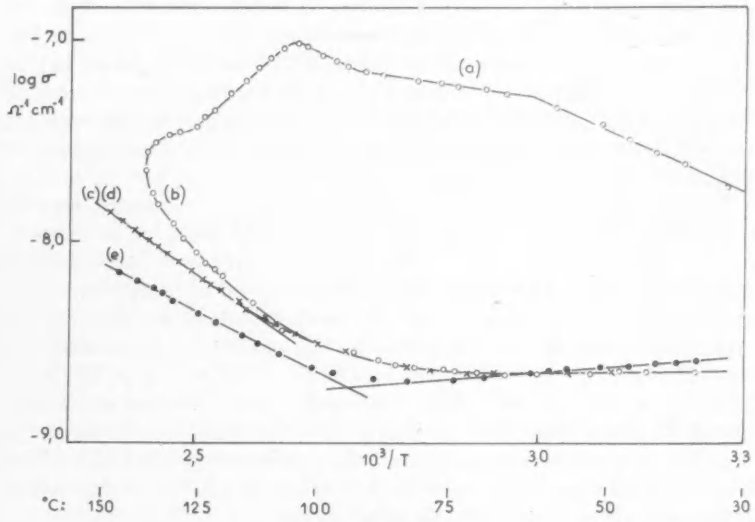


Fig. 6. Allures anormales de la variation de la conductivité en fonction de $10^3/T$: (*a*) premier chauffage; (*b*) premier refroidissement; (*c*) deuxième chauffage; (*d*) deuxième refroidissement; (*e*) variation reproductible.

Les premiers résultats que nous avons obtenus sont représentés sur le Tableau IV.

Discussion des Résultats Expérimentaux

Résistivités

La résistivité à 25°C varie selon les polymères examinés de 1 à 3 $\times$ 10^{10} ohm-cm sans qu'il y ait de relation nette entre la résistivité et le pourcentage de doubles liaisons conjuguées. Les valeurs obtenues sont relativement élevées. Cependant, comme il est difficile d'affirmer que la résistivité

mesurée soit la résistivité intrinsèque, nous ne chercherons pas à en interpréter les valeurs en fonction des paramètres structuraux.

Northrop[28] et Rosenberg[29] ont montré que lorsqu'on compare les mesures effectuées sur un même produit, en film, en monocristal ou en pastille de poudre polycristalline, on obtient des résistivités qui varient notablement d'un échantillon à l'autre, alors que les valeurs des énergies d'activation sont sensiblement les mêmes. C'est pourquoi nous nous sommes surtout intéressés aux valeurs de l'énergie d'activation qui semblent plus sûres que les valeurs des résistivités.

Energies d'Activation

Nous avons vu que les produits étudiés sont caractérisés par deux énergies d'activation. Alors que les valeurs de ΔE_1, relatives aux températures inférieures à la température critique T_c, sont en général très faibles et ne dépendent pas du taux d'insaturation, les valeurs de ΔE_2, que l'on observe pour des températures supérieures à T_c, décroissent quand le taux d'insaturation augmente (Tableau IV). Ainsi pour un polymère qui ne possède que 6% de motifs élémentaires déhydrochlorurés la valeur de ΔE_2 est de 2,79 eV alors qu'elle est de 0,87 eV pour un taux d'insaturation de 43% et de 0,70 eV pour un taux de 74%.

Lorsque, dans le domaine des semi-conducteurs, on rencontre, pour un même échantillon, deux énergies d'activation différentes, on attribue en général l'énergie d'activation la plus faible à la présence d'une impureté dans l'échantillon. Le chlorure de Li et le DMF sont les impuretés les plus vraisemblablement présentes dans nos produits. Mais on constate que l'addition de 10% de ClLi au polymère 177 ne diminue pas la valeur de ΔE_1 (n° 16, 177 + 10% ClLi, $\Delta E_1 = 0{,}12$ eV; n° 17, 177 pur, $\Delta E_1 \sim 0$). D'autre part, le DMF est volatil; l'échantillon, préalablement séché, reste plus de 72 heures sous vide poussé avant d'être soumis au cycle thermique final des mesures électriques, qui sont alors toujours reproductibles. Nous ne pensons donc pas que la présence de DMF ou de LiCl puisse être rendue responsable de la faible valeur de ΔE_1.

On peut proposer une autre explication pour rendre compte de l'invariance, ou de la faible variation, de la conductivité en dessous de T_c. Si l'on admet qu'à côté de la conduction σ_p à l'intérieur des grains il existe une conduction σ'—qui pourrait par exemple être une conduction superficielle à la surface des grains de polymère—on peut admettre qu'en dessous de T_c on mesure $\sigma' \gg \sigma_p \cdot \sigma_p$ augmentant de façon exponentielle avec la température, il arrive un moment où elle devient supérieure à σ', et, au-dessus de T_c, c'est la variation de σ_p que l'on observe. Cette hypothèse a l'avantage d'expliquer pourquoi, à température ambiante, on note une résistivité sensiblement égale pour le PVC pur et les produits déhydrohalogénés. Pour obtenir la résistivité intrinsèque à température ambiante, il suffirait de prolonger la droite de pente ΔE_2. En procédant ainsi, on s'aperçoit qu'à température ordinaire, la conductivité du PVC est de plusieurs ordres de grandeurs inférieure à celle des produits insaturés. Cependant, cette

hypothèse demanderait à être précisée, car on ne voit pas comment expliquer la conductivité superficielle élevée que nous avons fait intervenir.

Une troisième hypothèse consiste à envisager le polymère polyénique comme une solution solide de séquences déhydrohalogénées dans le chlorure de polyvinyle amorphe. Northrop et Simpson[30] ont étudié la variation de la conductivité de solutions solides d'anthanthrène dans trois solvants moins conducteurs. Ces solutions solides présentent également deux énergies d'activation. Celle relative aux basses températures est caractéristique du soluté, celle des hautes températures du solvant. La température de transition entre les deux énergies ne dépend que de la concentration du soluté.

Il ne semble pas que le cas de nos polymères puisse se ramener à celui de telles solutions solides. En effet, les ΔE_2 que nous observons, au lieu de rester constants, diminuent au fur et à mesure que la teneur en doubles liaisons augmente. Le ΔE_2 est donc caractéristique du polymère étudié. Par ailleurs, la température de transition T_c qui ne devrait dépendre que de la concentration en soluté, ne varie pas de façon systématique avec le degré de déhydrohalogénation. Il semble donc que cette explication soit trop simple et que l'hypothèse qui consiste à admettre que les deux énergies d'activation sont caractéristiques des deux types de structure chimique présents dans l'échantillon ne corresponde pas à la réalité—surtout quand l'on remarque que l'on obtient également deux droites sur des échantillons de PVC purs.

Dans ce dernier cas, on s'aperçoit que la température T_c est très voisine de la température de transition vitreuse T_g du PVC. Il serait donc possible que le changement de pente observé dans nos échantillons soit lié au passage du PVC de l'état vitreux à l'état fondu. Pour pousser plus loin cette explication, il faudrait être sur, qu'à toute température, on n'est pas dans le domaine d'absorption Debye, ce qui exigerait des mesures dans une gamme étendue de fréquences.

IV. CONCLUSION

Dans ce travail, nous ne prétendons pas présenter un semi-conducteur organique doué de propriétés remarquables. Mais les résultats de nos recherches permettent d'envisager favorablement une étude systématique des propriétés de polymères portant de longues séquences polyéniques.

En effet, la méthode de préparation que nous préconisons conduit à la formation, sur la chaîne, de très longues séquences de doubles liaisons conjuguées. Exempte de réactions parasites de pontages, de cyclisations et de substitutions, si fréquentes en pareil cas, la déhydrohalogénation du PVC par le système LiCl–DMF conduit à des polymères largement insaturés et bien définis.

L'étude préliminaire des propriétés électriques de ces produits nous autorise à les ranger parmi les semi-conducteurs organiques. Les électrons π des séquences de doubles liaisons conjuguées sont délocalisés et confèrent

aux échantillons les propriétés observées de conduction à température élevée. L'énergie d'activation peut être reliée au taux d'insaturation et est notablement plus faible que celle du PVC non traité. Il reste à déterminer le mécanisme de la conduction électrique et à le relier à la structure chimique du polymère: ceci exigera de compléter nos mesures en faisant varier la fréquence, le taux d'insaturation, et, à taux d'insaturation égal, la longueur des séquences de doubles liaisons conjuguées.

Nous tenons à exprimer notre très vive gratitude à M. le Professeur Charles Sadron, Directeur du C. R. M. et à M. le Professeur Henri Benoît, Directeur-Adjoint, pour le vif intérêt qu'ils ont manifesté à ce travail et pour les conseils qu'ils nous ont prodigués.

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Résumé

Les synthèses ne permettant pas d'accéder à de longues chaînes de doubles liaisons conjuguées, nous nous sommes attachés à créer des séquences polyéniques sur une macromolécule existante, par une réaction d'élimination. Les halogénures de polyvinyle se prêtent aisément à de telles réactions. Nous avons cherché à obtenir des produits aussi bien définis que possible. Nous n'avons donc pas eu recours à la déhydrohalogénation thermique qui conduit à des produits fortement réticulés, ni à l'élimination d'hydracide par action de bases organiques, ces dernières étant susceptibles de donner, à côté de la réaction attendue, une réaction parasite de substitution sur la chaîne. Nous avons provoqué la déhydrohalogénation des halogénures de polyvinyle par le chlorure de lithium—ou d'autres sels—en solution dans le DMF. Nous avons ainsi obtenu de très longes chaînes de doubles liaisons conjuguées qui présentent une absorption dans le visible au voisinage de 550 mμ et confèrent au polymère une couleur violet foncé. Nous avons essayé de comprendre le mécanisme de cette réaction et avons attribué à l'ion Cl^- le rôle de base forte en milieu DMF. Nous avons effectué des mesures de conductivité sur les produits ainsi obtenus. Les résistivités à température ambiante sont relativement élevées. Mais les énergies d'activation décroissent lorsque le taux d'insaturation des produits augmente, ce qui exprime la présence sur la chaîne, en quantités croissantes. d'électrons délocalisés.

Synopsis

Macromolecular chain molecules bearing long sequences of double bonds cannot be readily obtained by polymerization reactions, but it is possible to create such unsaturated blocks on suitable saturated polymers by an elimination reaction. It appears that polyvinyl halides are quite suitable for this purpose. We tried to get compounds as well defined as possible. Therefore, we did not use thermal dehydrohalogenation, as it usually yields crosslinked samples, nor the elimination by means of organic bases, which leads to substitution side-reactions. Lithium chloride (and some other salts) is quite effective, in dimethylformamide solution, on polyvinyl halides; this reaction, if carried out at moderate temperature, creates very long polyenic sequences on the PVC macromolecules. These substances are usually dark violet powders and exhibit strong light absorption near 550 mμ. To elucidate further the dehydrohalogenation mechanism we have carried out systematic experiments, and we have been able to show that the chloride anion behaves in DMF solution as a strong base, and is responsible for the observed reaction. Electrical conductivity measurements have been undertaken on our dehydrohalogenated polymers at constant frequency (1592 cycles/sec.). Resistivities at room temperature are quite high, but typical semiconductive behavior has been observed for their thermal variation. The activation energies have been found to decrease with increasing insaturation.

Zusammenfassung

Makromolekulare Ketten mit langen ungesättigten Sequenzen sind nicht leicht durch Polymerisationsreaktionen herzustellen. Wir haben deshalb versucht konjugierte Doppelbindungen auf einer anfangs gesättigten Kette durch Abspaltung aufzubauen. Polyvinylchlorid ist für solche Experimente gut geeignet, und wir haben danach gestrebt, dass wir möglicherweise gut definierte Substanzen bekämen. Da die thermische Chlorwasserstoffabspaltung zur Vernetzung der Proben führt, haben wir diese Methode ausgeschaltet. Die Wirkung der organischen Basen auf Polyvinylchlorid ist auch nicht eindeutig, da Substitution neben der erwarteten Abspaltungsreaktion auftritt. Wir haben Polyvinylhalogenide mit Lithiumchlorid (oder anderen Salzen) in Dimethylameisensaüreamid (DMF) versetzt und erhielten auf diesem Wege Polymere die sehr lange ungesättigte Blöcke enthalten. Diese Polymere sind als dunkel-violette Pulver ausgefällt worden und zeigen eine starke Lichtabsorption bei 550 mμ. Wir haben versucht, durch systematische Experimente, den Reaktions-mechanismus dieser Abspaltung zu erreichen. Die starke Basizität des Chlor-anions in DMF-lösung ist für die Bildung der Blöcke konjugierter Doppel-bindungen verantwortlich. Leitfähigkeitsmessungen wurden an einigen unserer Proben in Wechselstrohm (1592 Hz) durchgeführt. Obwohl die Leitfähigkeit als sehr klein erscheinen kann, besitzen die ungesättigten Polymere einen ausgesprochenen Halbleiter-charakter. Die Aktivierungsenergien sind klein und nehmen mit steigendem Unsättigungsgrad ab, was nur durch die Anwesenheit zahlreicher freier Elektronen erklärbar ist.

Discussion

M. Krysewski (*Lodz, Poland*): Je voudrais signaler que dans les études faites sur les polyacrylonitriles (PAN), j'ai trouvé des changements de valeur d'énergie d'activation ΔE [variation de la conductivité en fonction de $(1/T)$] dans la température T, très voisine de la température de transition vitreuse T_g. J'ai étudié les PAN irradiés avec de la lumière ultraviolette ainsi que des polymères avec des composés aromatiques possédant des éléctrons mobiles, p. ex. anthracène et ses dérivés. Les conductivités des échantillons ont été mesurées à l'air et sous vide (en forme de films). Ce n'est qu'à partir de quelques chauffages que la courbe log σ en fonction de $(1/T)$ a un comportement reproductible. Les détails de cette étude sont sous presse dans *Plaste und Kautschuk*. Il faut remarquer que cette température de la transiton dépend du taux de la conversion (de l'insaturation) et du contenu des composés aromatiques. L'hypothèse de J. P. Roth semble être très interessante et les études que lui et nous voulons exécuter, donneront plus de détails liés au passage du PVC et PAN de l'état vitreux à l'état fondu.

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Sur la Nature des Centres Paramagnétiques Detectés par RPE dans les Polymères Conjugués

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INTRODUCTION

Il a été constaté depuis quelques années qu'un grand nombre de polymères conjugués—peut être tous—présentaient un signal derésonance paramagnétique electronique (RPE) traduisant la présence de spins libres dont la concentration peut aller jusqu'à 10^{21} par gramme.

Tous les spectres ont des caractéristiques analogues; une seule raie assez étroite (5 à 10G) dont le facteur g présente toujours des écarts très faibles avec celui de l'électron libre (2,0023). L'absence de structure hyperfine malgré la présence fréquente dans ces polymères de noyaux dotés de spins nucléaires (H, N) les distingue des radicaux rencontrés dans les polymères saturés.[1] Les centres paramagnétiques sont vraisemblablement très délocalisés dans la chaîne du polymère. D'autre part il a été vérifié, par divers auteurs et par nous-mêmes, sur différents polymères conjugués solubles que le signal de RPE persistait en solution et, à l'intensité près, conservait les mêmes caractéristiques (facteur g, largeur de raie). Ce phénomène est donc une propriété de la macromolécule elle-même.

Il est à noter que ces polymères possèdent d'autres propriétés intéressantes: semi-conductivité, thermostabilité, propriétés catalytiques, bonne résistance aux radiations. Ces propriétés sont probablement dues[2] au grand nombre et à la délocalisation élevée des électrons π. Il en résulte en effet: (*a*) une diminution de l'énergie interne du système, d'où gain en stabilité: thermostabilité, résistance aux radiations; (*b*) un abaissement de l'énergie d'excitation des électrons π à l'état triplet, d'ou abaissement du "gap" entre les orbitales liantes et les orbitales antiliantes: propriétés semiconductrices et, pour certains auteurs, magnétiques.

Cependant, le problème de la véritable nature des centres paramagnétiques observés reste encore à élucider. Diverses interprétations ont été proposées. Nous allons rappeler les principales, puis les discuter.

LES DIVERSES INTERPRETATIONS

1. Electrons de Conduction Passés dans la Bande des Orbitales Antiliantes par Excitation Thermique

Le premier, Topchiev[3] explique le signal de RPE qu'il a observé dans du polyacrylonitrile pyrolysé en se référant à des travaux de Fletcher[4] con-

cernant la résonance d'électrons de conduction dans du silicium. Il se produirait un phénomène analogue à ce qui se passe dans les semi-conducteurs minéraux où des électrons venant, soit de la bande de valence, soit de niveaux d'impuretés passent dans la bande de conduction devenant ainsi paramagnétiques. La périodicité rencontrée dans les polymères permet également de définir une structure de bandes.[5] L'écart énergétique (ou bande interdite) entre la bande occupée la plus haute et la bande vide la plus basse est d'autant plus faible que le nombre de cellules de base est plus grand et que l'intéraction entre cellules est plus forte. Les premières orbitales thermiquement accessibles sont antiliantes et correspondent à des états triplets. Pour différents auteurs[6] l'excitation thermique d'électrons dans ces états triplets serait responsable du paramagnétisme. Cette conception trouve une illustration dans le comportement de certains semi-conducteurs organiques comme par exemple le complexe de transfert de charge iode–périlène[7–9] où, les électrons libres n'étant pas dégénérés, on vérifie effectivement que le nombre de spins libres et la conductivité varient ensemble de manière exponentielle en fonction de la température et avec la même énergie d'activation.

D'après cette interprétation, les porteurs de charge, dans la mesure où ils sont en concentration suffisamment faible pour ne pas être dégénérés, sont identifiables aux électrons célibataires responsables du paramagnétisme.

2. Electrons d'Etats Triplets Fondamentaux

Des mesures[10] du nombre de spins libres en fonction de la température dans la gamme 300–77°K sur des polymères conjugués ont montré que la susceptibilité suivait la loi de Curie. Ce fait, au moins dans l'intervalle de température étudié, contredit l'hypothèse d'électrons désappariés par excitation thermique. Certains auteurs[2] considèrent alors que pour des chaînes assez longues, la conjugaison et le nombre d'électrons π sont suffisamment élevés pour abaisser l'état triplet suffisamment près du fondamental pour être constamment peuplé dans toute la gamme de températures étudiées, ou même le rendre lui-même fondamental.

Il convient de dire que ces deux cas doivent être essentiellement différents. Le premier n'est qu'un cas particulier de l'interprétation 1 avecun "gap" très faible ($\ll kT$) entre états fondamentaux singulets et états triplets excités. Le second correspond à des macrobiradicaux stables. Des études à la fois expérimentales et théoriques[11,12] confirment que le niveau triplet s'abaisse à mesure que la longueur de la chaîne et le nombre d'électrons π augmentent. Il est donc concevable qu' au dessus d'une certaine longueur de chaîne, que nous appellerons longueur critique, l'état triplet se confonde avec un état fondamental. Ce processus établirait une relation étroite entre les deux possibilités envisagées. Une telle conception semble assez souvent admise. Nous verrons qu'elle soulève certaines objections.

3. Macroradicaux Stables

Winslow et collaborateurs[13–15] qui ont étudié les dérivés de pyrolyse du chlorure de polyvinyle et du polydivinylbenzène préoxydé considèrent que le signal de RPE est dû à des électrons non appariés provenant de valences libérées par évacuation de groupements volatiles lors de la pyrolyse. La structure résultante, bien que possédant une valence libre, serait stabilisée par l'énergie de résonance importante du système conjugué.

Ce modèle rapproche les polymères conjugués des charbons pyrolysés sur lesquels de nombreuses études ont été publiées.[16]

Plusieurs arguments militent dans ce sens. Le mode de préparation de plusieurs polymères conjugués qui consiste à traiter thermiquement un polymère non conjugué de manière à faire apparaître des doubles liaisons conjuguées par évacuation d'hydrogène (par exemple). Il faut cependant noter que des polymérisations directes à température ambiante conduisent à des polymères conjugués présentant des concentrations de spins libres comparables.

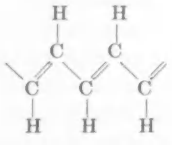
Les caractères des signaux de RPE obtenus sont très semblables: raie unique et étroite manifestant des effets de saturation pour de faibles puissances hyperfréquence.

Nous faisons rentrer dans cette catégorie toutes les interprétations qui font intervenir un nombre impair d'électrons π quel que soit le processus envisagé: (*1*) chaîne $CH_2—(CH)_{2n+1}—CH_2$ possédant intrinsèquement un nombre impair d'électrons π; (*2*) évacuation de groupements volatiles produisant un nombre impair de valences libres; (*3*) défauts dans la chaîne apparus lors de la polymérisation, qu'on peut considérer comme des sortes de niveaux d'impureté; (*4*) polymérisation s'arrêtant à un stade radicalaire et faisant apparaitre une valence libre en bout de chaîne, etc.

Dans tous ces cas on a affaire à des macroradicaux rendus stables par le haut degré de conjugaison et par empêchement stérique de recombinaison.

4. Défauts d'Alternance dans la Longueur des Doubles Liaisons

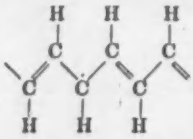
Dernièrement Pople et Walmsley[17] ont suggéré une explication possible du paramagnétisme des chaînes conjuguées. Ils traitent le cas d'une chaîne de polyène:



Les étapes de la discussion sont les suivantes. D'après des calculs de Ooshika[18] et Longuet-Higgins,[19,20] la configuration la plus stable d'une chaîne de polyène correspondrait non pas à des longueurs de liaison toutes égales, mais à des longueurs alternées deux à deux; de sorte qu'il faudrait faire intervenir entre atomes voisins deux intégrales de résonance β et β'

différentes. Il en résulte que la bande à moitié remplie par les électrons π doit être en fait scindée en deux bandes: l'une correspondant aux orbitales liantes pleine à 0°K, l'autre correspondant aux orbitales antiliantes vide à 0°K. Entre les deux, la bande interdite est d'autant plus large que la différence entre les deux liaisons est plus prononcée. Elle vaut $2\beta - \beta'|$.

Pople démontre mathématiquement l'existence de défauts d'alternance localisés et non liants dont le niveau d'énergie est situé au milieu de la bande interdite. De tels défauts peuvent être schématisés de la manière suivante:



Ils correspondent à une sorte d'état exciton et peuvent d'ailleurs être introduits de manière plus générale.[21] Ils sont paramagnétiques et, d'après Pople et Walmsley, ils doivent être décelables par RPE. D'autre part, bien que localisés, on doit les imaginer très mobiles dans la chaîne sous l'action des fluctuations thermiques; ce qui expliquerait l'étroitesse des raies de RPE et l'absence de structure hyperfine. Il faut noter que ces états correspondent à une certaine excitation de la molécule au dessus de l'état fondamental.

Cette interprétation serait caractérisée par un nombre de spins libres dépendant de la température et un nombre de spins libres/g indépendant de la masse moléculaire (dans la mesure où cette dernière n'est pas trop faible) du polymère étudié. En effet, de tels défauts auraient une certaine probabilité (dépendant de T selon la loi de Boltzmann) de se produire dans un intervalle donné de chaîne; par exemple,[17] un défaut tous les 70 atomes de C à 300°K. On voit ainsi que la longueur de la chaîne n'intervient pas.

La diversité des schémas proposés pour expliquer le paramagnétisme des polymères conjugués est assez révélatrice de la complexité du problème. La difficulté provient en premier lieu de la mauvaise définition physico-chimique des produits étudiés. Les formules chimiques ne sont souvent qu'hypothétiques; les polymères conjugués étant en majorité insolubles, les masses moléculaires sont la plupart du temps hors d'atteinte; mais de toute façon leur connaissance ne nous fournirait que des renseignements de caractère global. Il est absolument exclu d'avoir une connaissance exacte de la structure réelle de chaque chaîne, en particulier des irrégularités et des défauts qui peuvent avoir un rôle capital dans le phénomène qui nous intéresse. (L'idéal serait évidemment de disposer d'un monocristal parfait de polymère). Force est donc de recourir à des méthodes d'investigation indirectes. Dans la détermination de la nature des centres paramagnétiques observés dans les polymères conjugués,* nous avons pensé qu'il fallait pousser la recherche dans trois directions: (*a*) Une étude exhaustive des

* Il n'est pas certain que nous ayons affaire dans tous les cas à des centres paramagnétiques de même nature.

différents polymères conjugués doit dire s'il est possible d'établir une relation entre d'une part la formule, le degré de conjugaison, la masse moléculaire et d'autre part les paramètres de la RPE: largeur de raie, facteur g, temps de relaxation, et plus particulièrement nombre de spins libres. (*b*) Des études physiques de RPE doivent caractériser certains aspects des spins libres observés: la variation de leur nombre en fonction de la température, leur mode de relaxation, leur localisation et leur couplage au réseau. (*c*) Une étude de la corrélation entre les spins libres et d'autres phénomènes constatés dans les polymères conjugués doit permettre de préciser des propriétés de ces spins: en particulier leur rôle dans la semi-conductivité, la catalyse et l'adsorption. En outre, il est permis d'espérer que l'on puisse par ce biais jeter du même coup quelque lumière nouvelle dans la compréhension de ces phénomènes.

NOMBRE DE SPINS LIBRES EN FONCTION DE LA TEMPERATURE

Il importait en premier lieu de vérifier avec précision la variation du nombre de spins libres en fonction de la température et spécialement vers les basses températures.

1. Partie Expérimentale

Les mesures ont été effectuées sur un spectromètre RPE de haute sensibilité travaillant dans la gamme des 3 cm.[22] Deux échantillons de polyacrylonitrile pyrolisé ont été étudiés, tous deux pyrolisés sous atmosphère d'argon, le premier (a) à 250°C, le second (b) à 350°C. A température ambiante ces échantillons présentent des signaux de RPE traduisant la présence de 7×10^{18} spins libres/g pour (a) et de 5×10^{19} pour (b). Toutes les mesures ont été faites en comparant l'intensité du signal donné par l'échantillon à l'intensité du signal donné par un cristal de référence collé dans le fond de la cavité (un cristal de MgO dopé au Mn^{++} donnant 6 raies de résonance encadrant la valeur du g de l'électron libre).

Nous avons tracé des spectres à 300, 77, 4,2 et 1,2°K. Il a fallu tenir compte d'un effet très important de saturation du signal apparaissant pour des puissances hyperfréquence relativement faibles. Cet effet qui se manifeste au-dessus de 10^{-4} W à température ambiante et de 10^{-7} W à 1,2°K traduit un temps de relaxation spin-réseau T_1 très important (de l'ordre de 10^{-4} s à 300°K et 1 s à 1,2°K); ce qui signifie que les spins sont très faiblement couplés au réseau. Nous avons vérifié que pour les faibles puissances hyperfréquence, c'est à dire en l'absence de saturation, la largeur et la forme de la raie étaient indépendantes de la température. Pour chaque température nous avons tracé une série de spectres en faisant varier la puissance et nous avons porté les rapports PAN/Mn^{++} des amplitudes des raies obtenues sur l'enregistreur en fonction de la puissance. Afin d'éliminer l'influence de la saturation sur le signal la valeur symptotique de ce rapport a été adoptée pour chaque température. L'incertitude

sur les valeurs de ce rapport est évaluée à 10 % d'après la reproductibilité des mesures.

2. Résultats

Pour l'échantillon (a) d'une part et pour l'échantillon (b) d'autre part, les rapports des intensités des raies sont les mêmes à toutes les températures à mieux de 10% près. Admettant que le cristal de MgO dopé au Mn^{++} suit rigoureusement la loi de Curie jusqu'à 1,2°K, on peut conclure que nos échantillons (a) et (b) de PANP, dans la marge de la précision des mesures, suivent également la loi de Curie de 300 à 1,2°K: le nombre de spins libres est indépendant de la température; ils se trouvent dans des états fondamentaux et ne sont pas dégénérés. En toute rigueur, la précision des mesures nous permet de dire que si les spins libres correspondent à une excitation, celle-ci est inférieure à 10^{-5} eV–ce qui est extrémement faible.

DISCUSSION

Ce résultat obtenu sur deux échantillons de polyacrylonitrile pyrolysé et dans la mesure où il est généralisable à l'ensemble des polymères conjugués —ce que nous pensons—permet de discuter certains aspects des interprétations énoncées plus haut.

Il contredit les explications fondées sur une excitation thermique des chaînes macromoléculaires.

Les spins libres ne seraient pas identifiables aux porteurs de charges responsables des propriétés semiconductrices. Des mesures, précisément sur le polyacrylonitrile pyrolysé, donnent une énergie d'activation supérieure à 1 eV.

Il ne pourrait pas non plus s'agir comme le suggèrent Pople et Walmsley de défauts d'alternance dans les doubles liaisons qui correspondraient à des états excités. L'énergie d'activation requise pour la formation de tels défauts dans une chaîne de polyène idéale est aussi de l'ordre de l'électron-volt.

Si on admet une continuité dans l'abaissement du niveau triplet à mesure que la longueur de la chaîne augmente, des chaînes de longueur légèrement inférieure à la "longueur critique" (celle en dessous de laquelle le triplet est fondamental) donneront aussi un signal de RPE au-dessus d'une certaine température (d'autant plus basse qu'on est plus près de la "longueur critique").

Ainsi, étant donné qu'on a toujours affaire à des polymères de masse moléculaire plus ou moins dispersée autour d'une valeur moyenne, tout signal de RPE dans de tels polymères, puisque les expériences ne sont pas faites à 0°K, devrait être dû à la fois à des "spins fondamentaux" et à des "spins excités." Donc le nombre total de spins libres devrait décroître lorsqu'on abaisse la température jusqu'à ce qu'il n'y ait plus que les "spins fondamentaux" à 0°K.

En opérant sur des polymères de masse moléculaire (ou de conjugaison) assez faible, la décroissance du nombre de spins libres en fonction de T devrait être particulièrement sensible. C'est ce que nous avons essayé de vérifier en faisant nos mesures sur deux échantillons traités à des températures différentes, donc pour lesquels il est logique de supposer des degrés de conjugaison différents, et dont l'un présentait à température ambiante une concentration de spins libres 7 fois plus forte que l'autre.* Or nos résultats font apparaître des comportements en fonction de T absolument identiques pour les deux échantillons: le nombre de spins libres ne dépend pas de la température quel que soit le degré de conjugaison. Ce fait va à l'encontre de l'interprétation fondée sur un abaissement *progressif* des niveaux triplets à la hauteur du fondamental. Il reste cependant une issue pour conserver l'interprétation par états triplets fondamentaux; supposer que l'énergie d'activation, fonction de la longueur de chaîne (ou du degré de conjugaison) subit une discontinuité; elle passerait brusquement d'une valeur appréciable ($\gg kT$, telle que l'état triplet ne soit pratiquement pas peuplé à la température de l'expérience) à une valeur nulle. Ainsi on n'observerait que des spins fondamentaux. Un tel saut traduirait un changement qualitatif brutal dans la configuration électronique de la macromolécule, ce qui paraît assez peu vraisemblable.

Il y a une objection supplémentaire à l'explication du paramagnétisme par le modèle de l'état triplet abaissé à la hauteur du fondamental: dans une longue chaîne les niveaux étant groupés en bandes, si une bande s'abaisse jusqu'à rejoindre la bande des états fondamentaux, la structure de bandes rappellera celle des métaux où les électrons sont dégénérés et produisent un paramagnétisme (de Pauli) faible et indépendant de la température.

CONCLUSION

Il ne nous est pas possible dans l'état actuel de notre étude d'opter pour telle ou telle explication. Nous avons simplement voulu rappeler les interprétations proposées dans la littérature, puis, à la lumière de nos résultats partiels, discuter leur vraisemblance.

En résumé, il semble établi à notre avis que: (*a*) les centres paramagnétiques observés par RPE dans les polymères conjugués correspondent à des états fondamentaux; (*b*) le nombre de ces centres dépend du degré de conjugaison et de la longueur des chaînes.

Autrement dit: la conjugaison fait apparaître dans l'état fondamental un spin détectable par RPE. Poursuivant la discussion, on peut envisager deux possibilités: (*1*) La conjugaison facilite l'apparition de spins libres en stabilisant des structures à électrons non appariés auxquelles toutes sortes de processus (énumérés plus haut) peuvent donner naissance. (*2*) La conjugaison est directement responsable du paramagnétisme en faisant apparaître un spin résultant dans la macromolécule pour des raisons plus

* Des études[22] semblent avoir mis en évidence le fait que le nombre de spins libres est bien une fonction croissante du degré de conjugaison.

théoriques. En effet, il n'est pas interdit d'imaginer qu'une molécule puisse avoir un spin dans son état fondamental même si elle possède un nombre pair d'électrons π.

Sa fonction d'onde serait représentée au premier ordre par

$$\psi = \psi_0 + \lambda\psi_T$$

ψ_0 étant une fonction singulet et ψ_T une fonction triplet. λ est un coéfficient indépendant de la température (ce qui oppose ce schéma à celui de Pople et Walmsley) mais fonction (croissante) du degré de conjugaison et du nombre d'électrons π.

En d'autres termes, nous proposons de représenter l'état fondamental d'une molécule hautement conjuguée par une combinaison d'états singulet et triplet. Or, il est bien connu[24] que les éléments de matrices entre états de multiplicité différente sont nuls. En effet, les interactions dépendant du spin étant négligées en Chimie Quantique, la fonction d'onde doit être fonction propre de S^2, c'est à dire que la molécule doit être avec certitude soit dans un état singulet soit dans un état triplet. Cependant, des intéractions dépendant du spin existent certainement—en particulier des intéractions spin-orbite—et, en toute rigueur, l'Hamiltonien doit être complété de termes tenant compte de ces interactions. Alors l'objection précédemment soulevée tombe; un calcul de perturbations fait apparaître un coéfficient de mélange λ entre état singulet et état triplet. Physiquement cela signifie que si, à un instant donné, on effectue une mesure du spin de la molécule, on trouvera O avec la probabilité $(1 - \lambda^2)$ et 1 avec la probabilité λ^2. Ainsi les intéractions dépendant du spin individuel des électrons doivent donner naissance à un spin résultant dans la molécule. Une étude théorique doit dire si à partir d'un certain degré de conjugaison et d'un certain nombre d'électrons π, ce spin résultant peut être décelable par RPE.

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Résumé

La nature des centres paramagnétiques donnant un signal de RPE dans les polymères conjugués est encore mal élucidée. S'agit-il d'électrons de conduction passés dans une bande de conduction par excitation thermique, d'états triplets fondamentaux correspondant à des macrobiradicaux, de valences libres donnant des macroradicaux stabilisés par la haute énergie de résonance des polymères conjugués ou encore de défauts d'alternance dans les doubles liaisons? Nous rappelons ces différents modèles, puis, après avoir établi que les spins libres observés correspondaient à des états fondamentaux, nous les discutons.

Synopsis

The nature of the paramagnetic centers which give an electron paramagnetic resonance signal in conjugated polymers is not yet quite clear. Are they conduction electrons transferred in the conduction band by thermal excitation, or triplets in the ground state corresponding to macrobiradicals, or free bonds giving macroradicals stabilised by the high energy resonance of the conjugated polymers, or simply defects in the periodicity of the alternant bonds? We review here these various models, and discuss them after showing how it seems to us that the free spins observed correspond to ground states.

Zusammenfassung

Die Natur der paramagnetischen Zentren, welche in konjugierten Polymeren ein Elektronenresonanzsignal liefern, ist noch nicht völlig geklärt. Handelt es sich um Leitungselektronen, die durch thermische Anregung in das Leitfähigkeitsband gebracht wurden, um Triplets im Grundzustand, die Makrobiradikalen entsprechen, um freie, durch die hohe Resonanzenergie der konjugierten Polymeren stabilisierte Bindungen an Makroradikalen oder einfach um Defekte in der Periodizität der alternierenden Bindungen? Diese verschiedenen Modelle werden in der vorliegenden Arbeit besprochen und es wird gezeigt, dass die beobachteten freien Spins wahrscheinlich einem Grundzustand entsprechen.

Discussion

A. Rembaum (*California Institute of Technology, Pasadena, Calif.*): The line width of the ESR signal of numerous polymeric semiconductors has been reported to be of the order of 5–10 gauss. In several cases, however, the line width was found to be considerably greater. For example, the polyphthalocyanines are supposed to have a line width of 50–180 gauss, the polyphenyleneamino compounds 500–600 gauss, and for nucleic acids as much as 700–1000 gauss was claimed. Do you think there is a correlation between the line width of the ESR signal and conductivity?

M. Nechtschein: Nos mesures de la variation du paramagnétisme en fonction de la température semblent montrer, comme nous l'avons dit, que les spins libres ne viennent pas d'électrons de conduction car d'une part il ne sont pas dégénérés (ce ne sont pas des électrons métalliques) et d'autre part ils ne correspondent pas à une énergie d'activation (ce ne sont pas des éléctrons libres de semi-conducteurs).

Par ailleurs, nous pensons que s'il existe une corrélation entre la largeur de raie de RPE et la conductivité cela ne prouve rien quant à l'identité spinslibres-électrons de conduction: il se peut que d'une part la largeur de raie et d'autre part et *independamment* la conductivité depende d'un facteur intermédiaire, comme p. ex. le degré de conjugaison du systémé.

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Polydicyanoacetylene: Preparation and Properties

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Conjugated polymers are usually prepared by pyrolytic degradation of linear macromolecules. Polymers exhibiting the highest solid state conductance, e.g. "black Orlon," have been prepared in this way. However, polymers of this type with optimum qualities can only be prepared under extreme experimental conditions: heating to 400–500°C., in some cases in the presence of mineral salts.[1] It was assumed that products with better defined structures might be obtained by other methods, e.g., by a catalytic polymerization of suitable monomers.

The main work which was done in this field concerns the polymerization of alkyl and arylacetylenes.[2] In this paper the polymerization of dicyanoacetylene (DCA) (I), an acetylenic monomer containing electronegative substituents, is described.

$$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$$
I

The shape and volume of the nitrile group is just compatible with a fully planar configuration of the polymer chain which is necessary for a perfect conjugation.

We have found that DCA can be polymerized to black soluble polymers by anionic catalysts:[3] butyllithium, butylmagnesium bromide, monolithium benzophenone, and lithium naphthalene. Similarly to other polymerizations of acetylenes, the reaction requires a large amount of catalyst and is strongly exothermic; for the maintenance of constant temperature the catalyst had to be introduced stepwise into the reaction mixture. The polymerization was carried out by a standard procedure with various catalysts at −75°C.. and, in addition, with butyllithium in petroleum ether and tetrahydrofuran (THF) at 0°C. Precautions usual for anionic polymerizations were taken, especially concerning trace impurities and inert atmosphere. The polymer was isolated from the reaction mixture by evaporation of solvent and unreacted monomer. If lithium naphthalene and monolithium benzophenone were used as initiators, naphthalene, or benzophenone were removed by extraction.

With butyllithium the polymerization is induced by the addition of the catalyst to the monomer; the presence of the butyl group in the polymer was proved by infrared spectra. With lithium naphthalene and Li benzophenone the initiation takes place by electron transfer; naphthalene and

benzophenone are not attached to the polymer molecule and can be isolated quantitatively. In all cases studied, conversion is directly proportional to the amount of the catalyst (Fig. 1). The molar ratio of monomer

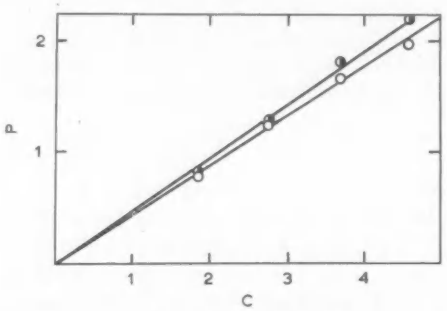
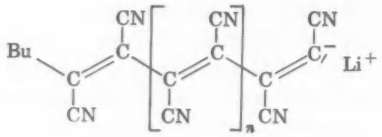


Fig. 1. Polymerization of DCA. Polymer yield P (g.) obtained from 1.94 g. of monomer. Polymerization induced by a solution of C mmoles of butyllithium in 5 ml. petroleum ether was performed in (○) THF (14 ml.) at −75°C. and (◑) in petroleum ether (14 ml.) at 0°C.

consumed to the total amount of catalyst added is independent of the initial ratio of reaction components. This ratio changes but little under different reaction conditions; in all our experiments its value lay between 5 and 6. The large amount of catalyst and the low degree of polymerization is not surprising in view of previous experience with polymerizations of other acetylenes.[2,4,5] According to Berlin's hypothesis, in the growing conjugated system gradual degeneration of the active center takes place as a result of resonance stabilization.

The basic structure of the polymer is supposed to be an anion of polycyanopolyene:



II

The presence of a large amount of nitrile groups is indicated by the infrared spectrum, so that cyclopolymerization to a structure analogous to "black Orlon" does not take place to a large extent during polymerization, nor by subsequent heating to 200°C. The polymer dissolves to a brownish-black solution in water and in polar organic solvents: methanol, ethanol, acetone, THF, etc. Solutions in water and in acetone are electroconductive (Fig. 2). Paper electrophoresis at pH 4.6 and 8.4 shows that the conjugated system is an anion.

The black polymer may be precipitated from aqueous solution by salts of Ag^+, Me_4N^+, and Cu^{++}. Similar properties were observed in cyanocarbons and their salts[6,7] which have a structure similar to the proposed structure of our polymer.

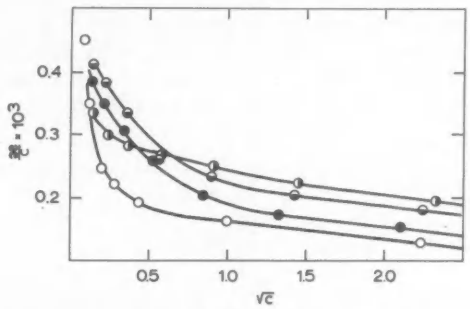


Fig. 2. Solution conductivity of polydicyanoacetylene. Conductivity concentration ratio κ/c of water solution of polydicyanoacetylene as a function of $c^{1/2}$, where c is concentration of the polymer expressed in g./l., and κ the conductivity in ohm cm. Catalyst, solvent, and temperature of polymerization were as follows: (○) butyllithium, THF, 0°C.; (●) monolithium benzophenone, THF, −75°C.; (◒) butyllithium, THF, −75°C.; (◑) lithium naphthalene, THF, −75°C.

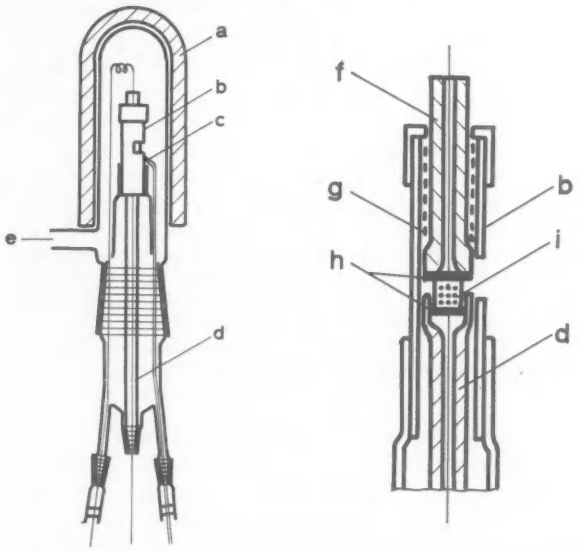


Fig. 3. Apparatus for measurement of the electrical conductivity: (*a*) shielding heating jacket; (*b*) brass holder of the electrodes; (*c*) Cu–Fe thermocouple; (*d*) silica capillary tube; (*e*) glass jacket connected with the source of high vacuum (10^{-5} mm. Hg.); (*f*) glass capillary tube; (*g*) temperature-resistance spring; (*h*) Pt electrodes (*i*) sample pellet.

The molecular weight determined by the ebulliometric method in acetone amounted to 400–500 for various samples. The value of this finding is limited by the presence of lithium ions in the sample, as well as by the possibility of association of the polymer anions.[7]

The electrical conductivity in the solid state was measured in pellets prepared from powdered samples by pressing under a pressure of several hundred kilograms/square centimeter. The pellet was placed between platinum disk electrodes (Fig. 3). Conductivity measurement was made in high vacuum (at least 10^{-5} mm. Hg) by DC voltage. Temperature

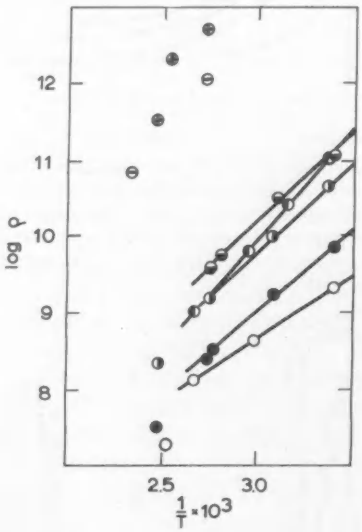


Fig. 4. Electrical resistivity ρ (ohm. cm.) of compressed pellets of polydicyanoacetylene as a function of inverse temperature for polymers obtained at various conditions (catalyst, solvent and temperature of polymerization given): (○) lithium naphthalene, THF, −75°C.; (●) Ag salt of the polymer obtained by butyllithium in THF at −75°C.; (◒, ◑) butyllithium, THF, −75°C.; (◐) monolithium benzophenone, THF, −75°C.; (⊖) butyllithium, petroleum ether, 0°C.; (⊕) butyllithium, THF, 0°C.

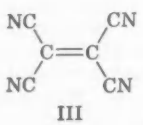
dependence of the resistance was measured up to 130°C. Prolonged heating at higher temperatures leads to irreversible changes accompanied by increased conductivity. Figure 4 shows the dependence of log ρ versus $1/T$ for samples prepared with different catalysts at various temperatures. From this dependence the activation energy is found to be in the range 0.64–1.12 e.v. and the specific resistance $\rho_{20°C.} = 10^{9}$–10^{12} ohm cm., depending on the method of preparation. Samples prepared at lower temperatures show higher conductivity. The reproducibility of the determination of activation energy is higher than the reproducibility of the absolute

Fig. 5. ESR spectrum of polydicyanoacetylene.

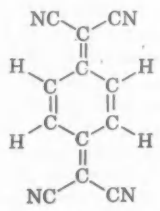
values of specific resistance. This may be caused by the lower reproducibility of the preparation of the pellet sample.

Polydicyanoacetylene is paramagnetic. All samples give a single narrow signal in the ESR spectrum with an intensity of 10^{18}–10^{19} free spins/g. and width about 7 gauss. No fine structure could be observed either in the solid state or in solution (Fig. 5).

A complete explanation of these phenomena has not been presented so far. In analogy with the cyanocarbons, an explanation based on the theory of electron donor–acceptor complexes is proposed. This agrees with the observation that the most active acceptors prepared, i.e., tetracyanoethylene (III) and tetracyanoquinodimethane (IV), contain, like our samples, nitrile groups bound to a conjugated system.



III



IV

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Synopsis

Synthesis of conjugated polymers by direct catalytic polymerization of suitable monomers is studied. Polymerization of dicyanoacetylene (DCA) with which formation of polymers analogous to the well-known "black Orlon" could be expected, is described in detail. DCA polymerizes by the action of anionic polymerization catalysts. The reaction is strongly exothermal and requires a large amount of catalyst. The method of gradual addition of the catalyst to the solution of the monomer was therefore adopted. Under these conditions a low molecular weight polymer (M.W. $< 10^3$) is formed, and the conversion is directly proportional to the amount of the catalyst (butyllithium). With Li-naphthalene or benzophenone-Li-ketyl initiation by electron transfer was observed, as neither naphthalene nor benzophenone is bound to the polymer. The polymer has apparently the structure of polycyanopolyene, as strong CN absorption is found in the infrared spectrum, persisting up to 200°C. The polymer is soluble in water and in polar organic solvents. It is paramagnetic; the ESR spectrum shows a single narrow signal (7 gauss) without any fine structure. Electric conductivity in the solid state was measured in pressed disks between Pt electrodes under pressure in high vacuum. Conductivity at room temperature σ_{20} was found to be in the range 10^{-9}–10^{-12} ohm^{-1} cm.$^{-1}$, and the activation energy ($E/2kT$) was 0.8–1.2 e.v., differing according to the method of synthesis.

Résumé

On a étudié la synthèse des polymères conjugués par polymérisation catalytique directe des monomères appropriés. La polymérisation du dicyanoacétylène (DCA) avec lequel on peut s'attendre à la formation de polymères analogues à l'orlon noir, a été décrit en détail. Le DCA polymérise par l'action de catalyseurs de polymérisation anionique. La réaction est très exothermique et nécessite une grande quantité de catalyseurs. On a adopté l'addition graduelle de catalyseur à la solution de monomère. Dans ces conditions un polymère de bas poids moléculaire se forme (m. w. $< 10^3$) et la conversion est directement proportionnelle à la quantité de catalyseur (butyllithium). Avec le Li-naphtalène ou le benzophénone-Li-cétyle on observe une initiation par transfert d'électrons et ni le naphthalène ni le benzophénone ne sont liés au polymère. Le polymère semble avoir la structure du polycyanopolyène (I), et on trouve dans l'infra-rouge une forte absorption du groupement CN, qui persiste jusqu'à 200°C. Le polymère est soluble dans l'eau et dans les solvants organiques polaires. Il est paramagnétique, le spectre EPR montre un seul signal étroit (7 gauss) sans aucune structure fine. La conductivité électrique à l'état solide a été mesurée sur des disques pressés entre des électrodes en platine sous pression et sous vide. La conductivité à température de chambre σ_{20} était de l'ordre de 10^{-9} à 10^{-10} ohm^{-1} cm^{-1}, et l'énergie d'activation ($E/2kT$) était de 0.8 à 1.2 e.v. suivant la méthode de synthèse.

Zusammenfassung

Es wurde die Herstellung von konjugierten Polymeren durch direkte katalytische Polymerisation geeigneter Monomerer untersucht. Die Polymerisation von Dicyanoacetylen (DCA), bei der die Bildung eines dem bekannten, sogenannten schwarzen Orlon analogen Polymeren erwartet werden konnte, wird eingehend beschrieben. DCA polymerisiert mit anionischen Polymerisationskatalysatoren. Die Reaktion ist stark exotherm und erfordert eine grosse Katalysatormenge. Daher wurde der Katalysator schrittweise zur Lösung des Monomeren zugesetzt. Unter diesen Bedingungen entsteht ein Polymeres niedrigen Molekulargewichts (M.G. $<10^3$) und der Umsatz ist der Menge des Katalysators (Butyllithium) direkt proportional. Bei der Verwendung von Li-Naphthalin oder Benzophenon-Li-Ketyl erfolgt der Start durch Elektronenübertragung, denn weder Naphtalin noch Benzophenon werden an das Polymere gebunden. Das Polymere hat anscheinend die Polycyanpolyenstruktur, da man im IR-Spektrum eine starke, bis hinauf zu 200°C persistente CN-Absorption findet. Das Polymere ist in Wasser und polaren organischen Lösungsmitteln löslich. Es ist paramagnetisch und das EPR-Spektrum weist ein einziges schmales Signal (7 Gauss) ohne irgend eine Feinstruktur auf. Die elektrische Leitfähigkeit im festen Zustand wurde an gepressten Scheiben zwischen Platinelektroden unter Druck im Hochvakuum gemessen. Die spezifische Leitfähigkeit bei Raumtemperatur σ_{20} lag im Bereich von 10^{-9}–10^{-11} Ohm^{-1} cm^{-1} und die Aktivierungsenergie ($E/2kT$) betrug 0,8–1,2 EV, je nach dem Syntheseverfahren.

Discussion

A. Rembaum (*California Institute of Technology, Pasadena, Calif.*): I should like to express my agreement with your remarks concerning the lack of accuracy of the reported resistivity values of polymeric semiconductors. I think that a considerable improvement would result if the resistivity of amorphous materials were measured, as frequently as possible, as a function of pressure. It was already shown that in many cases the logarithm of the resistivity is directly proportional to the square root of pressure. Our studies also confirm this. It would be advisable to make electrical measurements up to about 50,000 atmospheres or higher and from the linear plot an accurate value of resistivity at zero pressure could be obtained by extrapolation. This procedure would also minimize errors due to nonuniformity and surface effects.

M. Beneš: I quite agree with this.

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Catalyse sur Polymères Présentant des Proprietés de Resonance Paramagnétique Électronique

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INTRODUCTION

Semi-Conducteurs Organiques

Depuis quelque temps la littérature abonde en travaux relatifs à la conduction électrique des corps organiques et en particulier des hauts polymères. Le terme de "semi-conducteurs organiques" leur a été appliqué poure la seule raison que leur conductibilité σ augmente avec la température et obéit à la loi:

$$\sigma = \sigma_0 \exp \{-E/RT\}$$

mais en réalité, ce terme est abusif et préjuge d'un mécanisme de conduction calqué sur celui des semi-conducteurs minéraux: apparition des niveaux électroniques de valence et de conduction, effet des impuretés etc. qui ne sont pas du tout prouvés dans le cas des corps organiques.

On a montré[1] que la conduction dans le naphthalène est bien de type électronique et pas du tout de type ionique, si bien qu'il faut admettre l'existence, dans certains corps organiques, de porteurs de charges électrons ou trous positifs respensables de la conductivité.

Les premiers exemples et aussi les plus simples de composés organiques semi-conducteurs, ont été trouvés dans les molécules aromatiques condensées et les phtalocyanines.

En ce qui concerne les molécules aromatiques condensées qui constituent une famille homogène, Inokuchi[2] a montré que la conductivité augmente et que l'énergie d'activation diminue avec le nombre d'électrons π ce qui semble mettre l'accent sur l'importance de ce type d'électrons dans le mécanisme de la semi-conduction.

On sait maintenant, après les travaux de Pohl[3] et Berlin,[4] que les polymères présentant un système de doubles liaisons conjuguées s'étendant à travers toute la molécule (dits eka-conjugués) sont aussi des semi-conducteurs et présentent un assez grand nombre de centres paramagnétiques électroniques (de 10^{16} à 10^{21} par gramme) pouvant, en première approximation, être assimilés à des électrons non appariés.

Bien que nous venions de souligner que le terme de semi-conducteurs appliqué aux corps organiques soit abusif, il était tentant de rechercher si les propriétés catalytiques des semi-conducteurs minéraux pouvaient s'étendre à leurs homologues organiques.

Catalyse Sur Semi-Conducteurs Mineraux

Hauffe[5] puis Roginskiĭ[6] ont introduit en catalyse une distinction entre différents catalyseurs minéraux, basée sur leurs propriétés electriques. Trois catégories ont été considérées: (*1*) les conducteurs; (*2*) les semi-conducteurs; (*3*) les isolants.

Dans la première catégorie on trouve les métaux; dans la deuxième un certain nombre d'oxydes métalliques et de métalloïdes (Si, Ge), dans la troisième des corps ioniques cristallisés ou amorphes sans charges mobiles dans la masse.

La catalyse sur semi-conducteurs minéraux a fait l'objet des travaux théoriques de plusieurs chercheurs, dont, en particulier, Wolkenstein.[7] Un rôle spécial y est dévolu aux porteurs de charge (électrons ou trous positifs) qui sont rendus responsables de la chimisorption.

Un grand nombre d'expériences ont été réalisées pour vérifier la théorie en agissant sur le nombre des porteurs par traitement thermique ou par dopage.[8,9] Dans toutes ces expériences les tests catalytiques ont été menés en utilisant des réactions de stoechiométrie simple telles que la décomposition du protoxyde d'azote et l'oxydation de l'oxyde de carbone.

Ces deux réactions sont considérées, à l'heure actuelle comme caractéristiques de l'action catalytique des semi-conducteurs minéraux.

Bien que le mécanisme de la décomposition soit probablement très complexe, certains auteurs étudient aussi la décomposition de l'eau oxygénée[10] et de l'acide formique.[11]

Le mécanisme de la décomposition de N_2O sur semi-conducteurs est probablement l'un des mieux explicités. Rappelons le schéma adopté[12]:

Catalyseur type *p:*

$$N_2O \rightarrow N_2 + O^- + \boxplus$$
$$2\,O^- + 2\,\boxplus \rightleftharpoons O_2$$
$$N_2O + O^- + \boxplus \rightarrow N_2 + O_2$$

Catalyseur type *n:*

$$N_2O + e^- \rightarrow N_2 + O^-$$
$$2\,O^- \rightleftharpoons O_2 + 2e^-$$
$$N_2O + O^- \rightarrow N_2 + O_2 + e^-$$

On explique ainsi clairement l'intervention des électrons ou des trous positifs dans le mécanisme de l'action catalytique par semiconducteurs minéraux.

C'est donc par assimilation des semi-conducteurs organiques avec ces derniers que nous avons testé l'activité catalytique des polymères "eka-conjugués"[13] et tout d'abord, vis-à-vis de la décomposition du protoxyde d'azote. Cependant, il était aussi intéressant d'envisager d'autres réactions dont le mécanisme sur semi-conducteur est moins bien établi et c'est ainsi que nous avons choisi la décomposition du cyclohexanol et l'isomérisation du butène−1.

Certains des polymères étudiés ont été décrits dans la littérature: polybenzimidazole,[14] polyacène-quinone,[3] polypyromellitimide.[16] Quant aux autres ils ont fait l'objet soit d'une mise au point poussée: polyacrylonitrile pyrolysé (PANP) soit de synthèses originales: produits de condensation du polyisoprène avec d'une part la benzoquinone (PIB) et, d'autre part le chloranile (PIC).

METHODES EXPERIMENTALES

1. Préparation des Polymeres

Polymères Connus

Le polybenzimidazole est obtenu suivant la méthode de Vogel et Marvel[14] en condensant la diamino 3,3′-benzidine avec le téréphtalate de phényle.

Les polymères de type polyacène-quinone ont été synthétisés suivant la technique décrite par Pohl,[3] en condensant l'anhydride pyromellitique (APM) sur divers hydrocarbures (anthracène, pyrène) en présence de chlorure de zinc.

Le melon est préparé par chauffage de mélamine sous atmosphère inerte.

Le polypyromellitimide est obtenu suivant Idris Jones, Ochinski et Rackley[15] par action de l'anhydride pyroméllitique sur la *p*-phénylènediamine dans la diméthylformamide.

b. Pyrolyse de Polyacrylonitrile

Pour présenter une activité catalytique, le PAN commercial doit au préalable être pyrolysé entre 250 et 300°C.

L'activité catalytique d'un solide étant directement liée à sa surface spécifique, il était important d'appliquer au polyacrylonitrile un traitement thermique susceptible de conserver la texture de ce catalyseur.

De nombreux travaux ont montré que le mode de chauffage a une influence importante sur l'évolution de la texture des solides et qu'on la conserve mieux si on opère par chauffages isothermes successifs.[4]

Des experiences preliminaires de pyrolyse du polyacrylonitrile à l'air ayant montré que les propriétés catalytiques disparaissent très vite lorsque la température de pyrolyse s'accroît, nous avons appliqué un traitement sous courant d'argon.

Le produit de départ était un lot de polyacrylonitrile en poudre fourni par Crylor, dont les grains observés au microscope électronique sont sphériques et de dimensions uniformes (diamètre 0,15 μ).

Les traitements thermiques étaient effectués de la manière suivante. La poudre est placée dans un récipient en silice. On effectue un vide dynamique afin d'éliminer totalement les traces d'oxygène et l'on porte à 150°C sous vide pendant 4 h (désorption de vapeur d'eau). On fait circuler l'argon et stabilise la température à 250 ± 1°C pendant 24 heures; on obtient le PAN 250. Le PAN 300 est obtenu en faisant subir le même traitement à un nouveau lot de produit de départ et en poursuivant le traitement du PAN 250 pendant 24 h à 300 ± 1°C. Ainsi, le PAN 500 a été soumis par paliers successifs de 24 h aux températures de 250, 300, 350, 400, 450 et 500°C.

Une expérience réalisée à 350°C montre l'importance du mode de traitement que nous avons adopté malgré son extrême lenteur. Un lot a été porté à 150°C sous vide pendant 4 h, puis directement à 350°C sous courant d'argon pendant 48 h. Alors que les échantillons de la première série conservent une surface de 3 m^2/g pour des températures comprises entre 300 et 450°C, celui-ci présente une surface inférieure au mètre carré.

c. Polycondensats de Polyisoprène avec les Quinones

La réaction de condensation du polyisoprène (*cis* 1.4) avec des quinones a été effectuée de deux manières différentes.

1. PIC. La condensation avec une quinone reactive comme le chloranile, peut être réalisée en solution. Pour cela on dissout 147,4 g de chloranile (0,6 mole) dans 750 ml de xylène chaud, puis on y ajoute une solution de 20.4 g de polyisoprène (0,3 mole) dans le même volume de xylène. On fait passer un courant d'azote dans la solution, et, en agitant continuellement, on porte à ébullition pendant 10 h. Le précipité noir qui est apparu est alors filtré à chaud, lavé et extrait par du benzène dans un soxhlet pendant 48 h. Il est enfin séché sous vide à 50°C. Le polymère obtenu est noir, il contient environ 5×10^{19} centres paramagnétiques par gramme, et présente un effet Seebeck positif de 0,20 mV/°C.

2. PIB. Avec une quinone moins active telle que la benzoquinone la réaction en solution est plus difficile. Une réaction intéressante a cependant pu être observée en supprimant le solvant de réaction. C'est ainsi qu'en ajoutant, sous une vigoureuse agitation 3,7 g (0,05 mole) de polyisoprène finement divisé à 162 g (1,5 mole) de benzoquinone fondue et maintenue à 145°C, on obtient après 4 h de chauffage sous courant d'azote, une volumineuse masse noire qui est extraite dans un soxhlet pendant 48 h par du benzène et 48 h par de l'alcool. Le produit noir obtenu, 93 g, est apparamment un polycondensat de benzoquinone: il contient aussi 5×10^{19} centres paramagnétiques par gramme.

3. Traitement Thermique. Un traitement thermique ultérieur, effectué dans un four thermostatisé à ±2°C sous atmosphère d'argon, a permis de déceler une transformation chimique des produits jusqu'à une température de 350°C: les polycondensats PIB contiennent alors 2×10^{21} centres paramagnétiques par gramme et présentent d'intéressantes propriétés de thermostabilité.

Une étude plus détaillée de ces produits sera publiée prochainement.[16]

2. Surface Spécifique des Catalyseurs

Les surfaces spécifiques ont été déterminées par la méthode classique de Brunauer, Emmett et Teller, d'adsorption d'azote à la température de l'azote liquide. Les valeurs des pressions partielles d'azote ont été choisies de manière à ce que le rapport pression partielle sur pression de vapeur saturante de l'azote à 77°K soit compris entre 0,07 et 0,25.

L'incertitude sur nos mesures, dans le domaine des surfaces comprises entre 1 et 30 m^2/g est de 10%. Les surfaces spécifiques inférieures à un m^2 ne peuvent être déterminées avec notre appareillage.

3. Conductivité des Polymères

Elle a été déterminée à 20°C sous atmosphère d'azote, au moyen d'un appareil Lemouzy Multi Dyne M.D.N. Les produits sont mis sous forme de pastilles (dont l'épaisseur est ensuite mesurée avec précision) en comprimant sous une pression de 5000 kg/cm^2 le polymère en poudre préalablement séché sous vide; le contact avec les électrodes est assuré par une couche (de peinture) d'argent déposée sur la pastille. L'effet Seebeck a été déterminé dans les mêmes conditions entre deux petites plaques chauffantes enserrant la pastille et ses électrodes, et commandées chacune par un système indépendant de régulation de température: le gradient de température est mesuré par des thermocouples encapsulés dans les électrodes.

4. Determination du Nombre de Spins Libres

Les déterminations ont été effectuées au laboratoire de résonance magnétique du Centre d'Etudes Nucléaires de Grenoble. La méthode expérimentale a été exposée, par ailleurs.[17]

Notons que l'incertitude sur les mesures relatives est de l'ordre de 10% et que la valeur absolue n'est donnée qu'à titre indicatif.

5. Test Catalytiques

a. Décomposition du Protoxyde d'Azote

Cette réaction est simple et on ne lui connaît pas de réactions secondaires. Elle se fait avec augmentation du nombre de molécules:

$$2\,N_2O \rightarrow 2\,N_2 + O_2$$

Par suite, une étude en appareil statique est la plus aisée.

Le protoxyde d'azote (air liquide) est purifié par condensation à la température de l'azote liquide.

La température du réacteur est régulée à ±1°C. Les dimensions du réacteur sont telles que le gradient de température est inférieur à 1°C. Le poids de catalyseur est voisin de 1 g.

Des études préliminaires ont montré qu'en opérant à 250° pendant un temps de réaction de 1 h 30, le taux de conversion du protoxyde d'azote était

faible (l'inhibition par l'oxygène formé est classique) et que dans ces conditions le vieillisement du catalyseur était négligeable.

La détermination de l'activité catalytique des échantillons a été effectuée de la manière suivant,[19] après avoir laissé le protoxyde d'azote à pression atmosphérique en contact avec le catalyseur porté à 250°C pendant 1 h 30, on mesure la pression de l'azote et de l'oxygène formés en condensant le protoxyde d'azote. Un manomètre à acide sulfurique permet des mesures précises même pour les très faibles taux de conversion.

b. Décomposition du Cyclohexanol

Le dispositif expérimental permet de travailler en régime dynamique. Le cyclohexanol préalablement purifié est introduit dans un réservoir terminé par un tube capillaire qui en assure un débit constant. L'alcool ainsi introduit dans la partie supérieure du réacteur est vaporisé au contact de billes de verre (qui servent aussi au préchauffage de la vapeur) puis traverse le lit catalytique porté à 350 ± 1°C.

Un piège permet de recueillir les produits condensables (cyclohexanol, cyclohexène et cyclohexanone) et de les analyser par chromatographie en phase vapeur. L'hydrogène formé est rassemblé dans un compteur à gaz à pression constante de type vase à débordement.

c. Isomérization du Butène

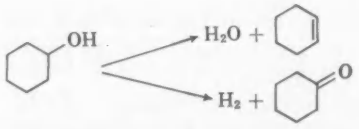
L'étude est effectuée en régime dynamique, sous faible débit de gaz (2 cc/min environ). Le catalyseur (1 g environ) est maintenu à la température de 300 ± 1°C. Les produits de l'isomérisation, *cis* et *trans*-butènes-2 sont analysés par chromatographie gazeuse.

RESULTATS

1. Catalyse par les Semi-Conducteurs Organiques

Nous avons pu montrer qu'un certain nombre de réactions, de caractères différents, sont catalysées par divers semi-conducteurs organiques: la décomposition du protoxyde d'azote, la décomposition des alcools, l'isomérisation du butène et l'oxydation de la tétraline.[19,20]

Le cyclohexanol présente la particularité intéressante de se décomposer suivant deux processus différents: une déshydratation et une déshydrogénation:



Cette réaction peut donc être utilisée comme critère de la sélectivité des catalyseurs au même titre que la réaction, souvent étudiée, de décomposition de l'acide formique.

Il est intéressant de rappeler que la plupart des oxydes métalliques accélèrent les deux réactions dans des proportions qui dépendent de leur nature chimique et de leur mode de préparation alors que la réaction de

TABLEAU I
Décomposition du Protoxyde d'Azote

Produit	Surface, m^2/g	Activité/ g	Activité/ m^2	Nombre de spins/g
PANP 350	3	1840	610	$5,0 \times 10^{19}$
Polybenzimidazole	1	300	300	$5,0 \times 10^{19}$
Polyacène-quinone[a] (APM)—anthracene	90	980	11	10^{21}
PIC 250	1,6	640	400	$4,2 \times 10^{20}$
PIB 250	<1	118	—	$1,7 \times 10^{21}$
Melon	13	0	0	$< 10^{16}$
NiO	5,7	890	156	

[a] La surface active de ce produit ne correspond certainement pas à sa surface mesurée. En effet, l'adsorption physique de l'azote est anormalement lente ce qui est généralement le fait des produits extrêmement microporeux.

TABLEAU II
Décomposition du Cyclohexanol

Produit	Surface, m^2/g	H_2O, %/g	H_2O, %/g	H_2, %/m^2	H_2O, %/m^2	Nombre de spins/g
PAN 350	3	0,83	1,11	0,28	0,37	$5,0 \times 10^{19}$
Polybenzimidazole	1	0,54	1,7	0,54	1,7	$5,0 \times 10^{19}$
Polyacène-quinone (APM—anthracène)	90	0	20	0	0,22	10^{21}
PIC 250	1,6	3,8	14	2,4	8,8	$4,2 \times 10^{20}$
PIB 250[a]	<1	8,9	5,4			$1,7 \times 10^{21}$
Pyromallitimide		0	0	0	0	$<10^{16}$
Polyacène-quinone (APM—pyrène)		29,4	24,5			6×10^{20}
Cr_2O_3		22,5	23,5			

[a] La surface spécifique de ce produit est nettement inférieure a 1 m^2/g et n'a pu être déterminée avec notre appareillage.

TABLEAU III
Isomérisation du Butène Normal

Produits	Teneur en *cis* et *trans* butènes-2, %
PIB 250	2,3
PIC 250	4
PANP 350	5
Polybenzimidazole	~0
AMP—anthracene	6,5

déshydrogénation se fait exclusivement à 100% sur les métaux et la réaction de déshydratation presque exclusivement sur les catalyseurs acides.

Les Tableaux I–III résument l'essentiel des résultats obtenus.

A titre comparatif, nous avons indiqué les activités catalytiques de quelques composés minéraux semi-conducteurs classiques.

On peut observer que, au moins certains des composés semi-conducteurs organiques que nous avons testés, présentent des activités catalytiques comparables et même supérieures à celles de ces semi-conducteurs minéraux. Il est alors permis de considérer qu'on se trouve véritablement en présence d'une nouvelle classe de catalyseurs.

En comparant les résultats des divers tableaux, on s'apercoit que les produits ont une activité catalytique et une sélectivité qui varient dans de larges mesures. Cette observation nous conduit à supposer une influence importante de la structure chimique de ces solides.

Une autre remarque générale peut être faite: tous les polymères qui offrent une activité catalytique décelable (dans nos conditions expérimentales) possèdent un grand nombre d'électrons non appariés (supérieur à 10^{17} par gramme), délocalisés dans leur molécule ainsi qu'en témoigne la valeur du facteur g.[18] Ainsi des produits comme le melon et le pyromellitimide dont on n'a pas pu déceler de signal de RPE ou dont la concentration en spins libres est certainement inférieure à 10^{16} n'ont présenté aucune activité catalytique.

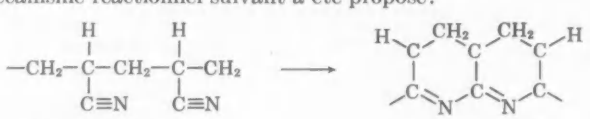
Comme nous avions, par ailleurs[20] vérifié le parallélisme entre l'activité catalytique et le nombre de centres paramagnétiques des polyacrylonitriles pyrolysés, il était intéressant de vérifier que ce parallélisme se manifestait pour d'autres séries de produits ayant des structures différentes et possédant des concentrations variables de spins libres.

2. Activité Catalytique et Nombre de Spins Libres

a. Polyacrylonitriles Pyrolyses

Les propriétés semi-conductrices du polyacrylonitrile pyrolysé sont connues depuis plusieurs années.[21,22] Le produit de départ, sous forme de poudre ou de fil blanc, chauffé à l'air ou sous atmosphère inerte (azote ou argon), à des températures comprises entre 200°C et 750°C, prend une couleur brun rouge à noire et présente des propriétés semi-conductrices, ainsi qu'un signal de résonance paramagnétique électronique intense.

Le mécanisme réactionnel suivant a été proposé:



et après déshydrogénation:

TABLEAU IV
Catalyse de la Decomposition de N_2O par le Polylacrylonitrile Pyrolysé

Temperature de pyrolyse, °C	Surface, m^2/g	Nombre de spins/g $\times 10^{-19}$	Activité catalytique
250	6.4	0.7	24.5
300	3	2	43
350	3	5	68
400	3	16	84
450	3	41	65
500	6	25	30

Une étude de la perte de poids du produit au cours du traitement thermique montre que ce mécanisme est possible. Les spectres infrarouges, effectués sur des pastilles au bromure de potassium, permettent de mettre en évidence la disparition des liaisons C≡N et l'apparition des liaisons C=N. Toutefois la preuve de la formation de cycles déshydrogénés n'a pas été apportée à notre connaissance.

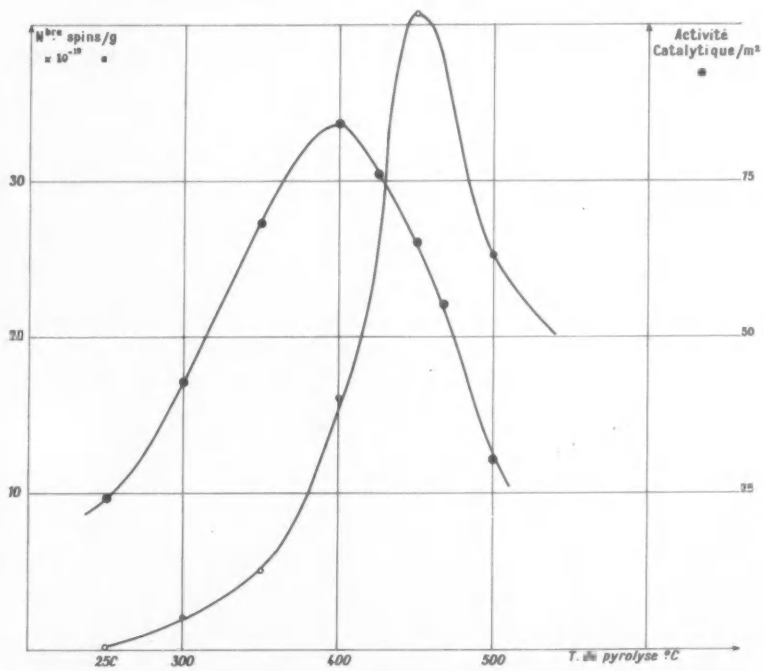


Fig. 1. Relation entre le nombre de spins libres et l'activité catalytique du polyacrylonitrile pyrolysé a différentes températures.

Les propriétés électriques du polyacrylonitrile pyrolysé varient avec la température du traitement thermique appliqué et nous avons effectué une série de pyrolyses à différentes températures comprises entre 250 et 550°C afin d'étudier l'influence de l'évolution des propriétés électroniques du polyacrylonitrile pyrolysé sur son activité catalytique.[20]

Le test d'activité catalytique choisi pour cette étude est la décomposition du protoxyde d'azote.

Sur le Tableau IV sont portées les valeurs expérimentales concernant la surface spécifique, le nombre de spins libres et l'activité catalytique des différents échantillons. Cette dernière grandeur est rapportée à l'unité de surface des échantillons.

On a porté sur un même graphique (Fig. 1) la variation de la concentration en spins libres et celle de l'activité catalytique en fonction de la température de pyrolyse. Le parallélisme dans la variation de ces grandeurs a été discuté par ailleurs.[20]

b. Produits de Condensation du Polyisoprene et de Quinones

Nous avons pu confirmer ce parallélisme par une étude analogue effectuée sur des produits originaux: les produits de condensation de polydiènes avec les quinones; une description de la structure et des propriétés physicochimiques de ces produits fera l'objet d'autres communications.[16,23]

Il est probable que dans un premier stade de réaction la quinone déshy

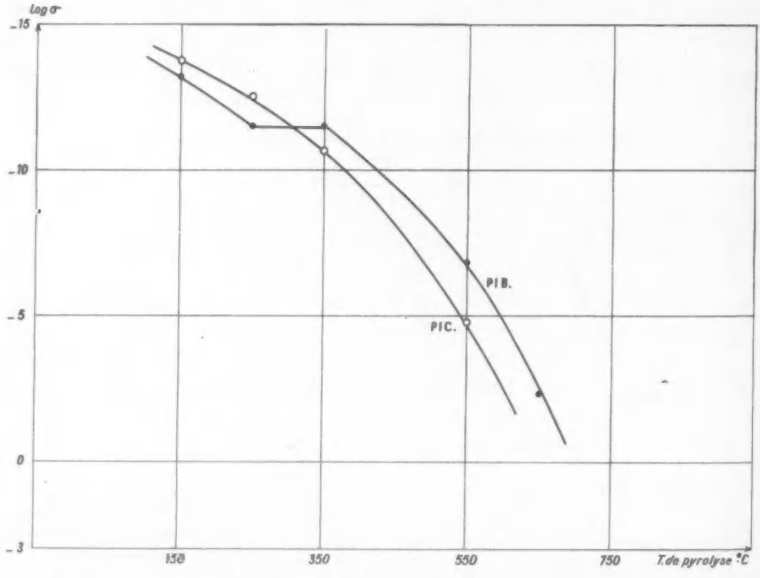
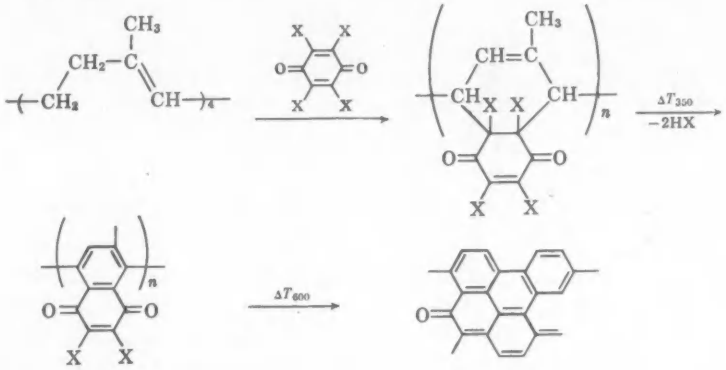


Fig. 2. Conductivité des produits de condensation du polyisoprène avec les quinones en fonction de la température du traitement thermique.

drogène le polymère qui subit alors une réaction de Diels-Alder; sous l'effet d'une élévation de température relativement modérée (jusqu'à 350°C environ), il y a sans doute une aromatisation des cycles formés; enfin à des températures plus élevées, le polymère doit subir une "pré-graphitisation" similaire à celle décrite par Winslow pour les polydivinyl-benzène oxydés:[24]



Pour la réaction entre l'isoprène et le chloranile, les deux premières étapes ont pu être confirmées par une étude comparative des variations de poids

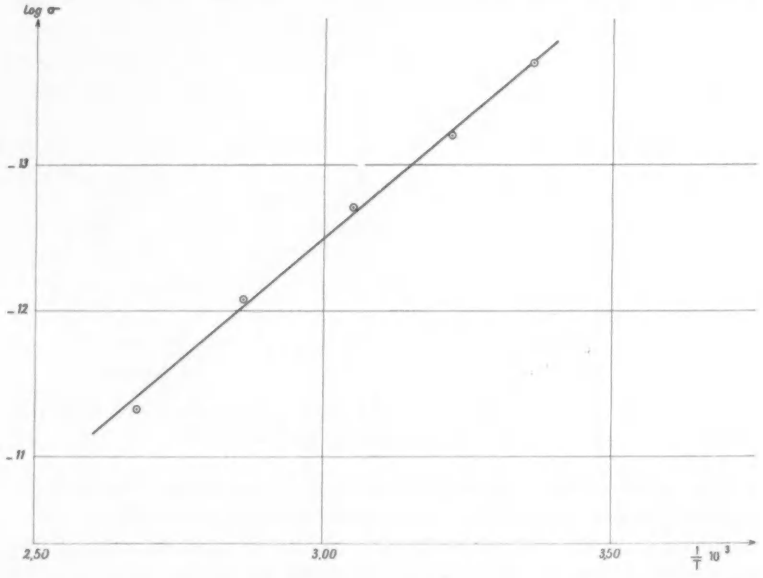


Fig. 3. Variation de la conductivité du produit de condensation de la benzoquinone (PIB), en fonction de la température de l'échantillon.

du polymère et du dégagement d'acide chlorhydrique pendant la synthèse et le traitement thermique; ces étapes doivent également s'accompagner d'une élimination des motifs isopréniques n'ayant pas encore réagi. La dernière étape de transformation de la molécule en un réseau de noyaux

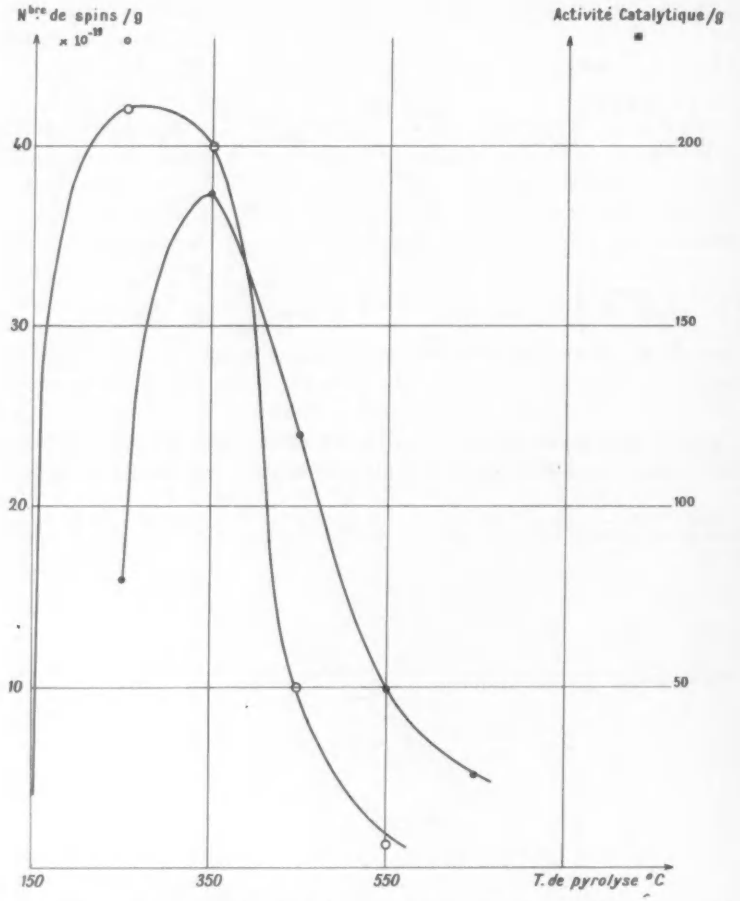


Fig. 4. Relation entre le nombre de spins et l'activité catalytique du PIC traité à différents températures.

aromatiques condensés est confirmée par l'augmentation brusque de la conductivité par traitement à des températures supérieures à 400°C, traitement qui n'est pas accompagné d'une variation de poids importante (Fig. 2).

La réaction du polyisoprène avec la benzoquinone fondue est probablement d'un type différent, une étude des rendements obtenus permet en

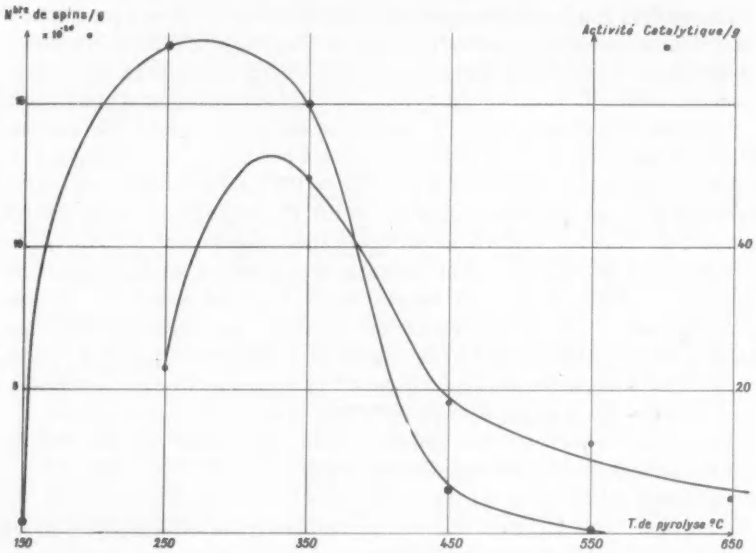


Fig. 5. Relation entre le nombre de spins et l'activité catalytique du PIB traité à différentes températures.

tout cas de conclure à une véritable homo-polycondensation de la benzoquinone initiée par le polyisoprène.

Ces produits ont des propriétés caractéristiques de semi-conducteurs organiques. Le logarithme de la conductivité varie linéairement en raison de l'inverse de la température de l'échantillon (Fig. 3), d'une manière qui permet de calculer une énergie d'activation de conduction de l'ordre de 0,62 eV.

Dès avant tout traitement thermique les polymères obtenus ont une concentration importante en centres paramagnétiques (5×10^{19}); leur activité catalytique et celle des produits résultant du traitement thermique sur la décomposition du N_2O paraît obéir aux mêmes facteurs que celle du polyacrylonitrile pyrolysé ainsi qu'on peut l'observer sur les Figures 4 et 5; l'activité catalytique y est rapportée à l'unité de poids, la variation de surface en fonction de la température de traitement étant relativement faible.

CONCLUSION

Au cours de ce travail nous pensons avoir clairement montré que les polymères eka-conjugués constituent une nouvelle classe de catalyseurs. La variété des réactions tests: décomposition de N_2O, déshydrogénation–déshydratation du cyclohexanol, et isomérisation du butène montre que leur domaine d'application est assez vaste et se recoupe assez bien avec celui, mieux connu, des semi-conducteurs minéraux.

Le résultat le plus intéressant est, à notre avis, celui qui concerne le parallélisme entre le nombre de centres paramagnétiques et l'activité catalytique. D'une part certains polymères ne présentant pa de centres (melon, pyromellitimide) n'ont pas d'activité catalytique et d'autre part, pour trois d'entre eux l'activité suit la variation du nombre de centres. Dans un domaine de températures compris entre 250 et 400°C pour le PANP et entre 300 et 550°C pour PIB et PIC, les polymères envisagés présentent un comportement opposé: le PAN pyrolysé à des températures croissantes voit ses centres paramagnétiques augmenter tandis que les condensats PIB et PIC voient au contraire ce même nombre diminuer. Malgré la modification probable de la structure chimique des chaînes polymériques, l'activité catalytique (vis-à-vis du N_2O) suit ces variations. Cette concommittance observée à trois reprises, laisse penser que l'influence du nombre des centres paramagnétiques, l'emporte de beaucoup sur l'influence possible des changements de structure.

Cependant ce facteur structural a une influence certaine qui se manifeste sur certaines de réactions catalytiques comme le montre l'étude de la déshydrogénation–déshydratation du cyclohexanol. Ce facteur structural est encore peu précis et son étude est en cours sur des catalyseurs dont on modifie systématiquement la structure.

Quant à la nature de ces centres, la valeur du facteur g 2,0023, semble indiquer qu'il s'agit d'électrons complétement délocalisés, mais ils sont loin d'être libres puisque, par ailleurs, la conductibilité est toujours très faible (exception faite pour les polyquinones PIB et PIC qui, après traitement à des températures élevées, ont une conductivité d'un type graphitique, bien que leur nombre de centres ait fortement diminué), ce qui confirme que, du point de vue électronique, on ne peut assimiler les polymères eka-conjugués et les semi-conducteurs minéraux.

Il nous semble aussi que l'on peut tirer un enseignement valable de la comparaison du type de réactions catalytiques et des propriétés électriques de ces polymères.

On sait, en effet que dans la plupart des cas où l'on a pu mesurer un effet Seebeck, celui-ci s'est rattaché à un effet de conduction par trous positifs, c'est-à-dire que, du point de vue électronique, les semi-conducteurs organiques seraient de type p. C'est également le cas des produits PIB et PIC, comme nous avons pu le vérifier nous-mêmes.

Si nous considérons maintenant notre étude sur la décomposition de N_2O nous voyons que le PANP, par exemple, présente une activité supérieure à celle du NiO, semi-conducteur p qui semble le meilleur des catalyseurs minéraux connus. Donc, de ce point de vue aussi, les semi-conducteurs organiques semblent agir comme des conducteurs p.

Bien que l'action catalytique de ces produits s'exerce sur des réactions qui s'expliquent généralement par un mécanisme de nature ionique, il semble difficile à l'heure actuelle de préciser davantage leur mode d'action. Nous avons simplement mis en évidence que cette activité est étroitement liée à la présence de certains centres paramagnétiques. Quels sont ces centres et comment agissent-ils? La question est entière, mais le problème est posé.

Les auteurs désirent adresser leurs remerciements a Madame A. C. Korn-Girard et Messieurs R. Sallé et B. Sillon qui ont effectué les synthèses et les déterminations structurales, a Monsieur M. Nechtschein pour les mesures de résonnance paramagnétique électronique ainsi que pour les fructueuses discussions qu'il a animées, et a Monsieur F. X de Charentenay pour les mesures électriques.

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Résumé

Certains polymeres synthétiques préparés par condensation de polymères non saturés avec le chloranile et la benzoquinone, présentent un signal de résonance paramagnétique électronique intense (le nombre de centres paramagnétiques par gramme peut atteindre 10^{21}); le polyacrylonitrile traité thermiquement est doué de la même propriété. Tous ces polymères ont présenté une activité catalytique notable vis-à-vis de la décomposition du N_2O, de la déshydrogénation du cyclohexanol et de l'isomérisation du butène-1. Pour tous ces produits un parallèle remarquable entre l'activité catalytique et le nombre de centres paramagnétiques a également pu être établi.

Synopsis

New polymers synthesized by condensation of unsaturated polymers (polydienes) with chloranil and benzoquinone exhibit a strong electron spin resonance signal (2×10^{21} spins/g.) comparable to that of thermally treated polyacrylonitrile. All these polymers

have a noticeable catalytic activity on the decomposition of N_2O, the dehydration of cyclohexanol, and the isomerization of 1-butene. An interesting parallel was established between the catalytic activity of all these products and their spin concentrations.

Zusammenfassung

Gewisse synthetische, durch Kondensation von ungesättigten Polymeren mit Chloranil und Benzochinon dargestellte Polymere liefern ein intensives Elektron-Spin-Resonanz-Signal (die Zahl der paramagnetischen Zentren pro Gramm kann 10^{21} erreichen); thermisch behandeltes Polyacrylnitril besitzt die gleiche Eigenschaft. Alle diese Polymeren zeigten eine merkliche katalytische Wirksamkeit bei der Zersetzung von N_2O, bei der Dehydrierung von Cyclohexanol und bei der Isomerisierung von Buten-1. Bei allen Produkten besteht eine bemerkenswerte Parallelität zwischen der katalytischen Wirksamkeit und der Zahl der paramagnetischen Zentren.

Discussion

M. Magat (*Faculté des Sciences, Orsay, France*): Dans quelle mesure pouvez-vous affirmer qu'une diminution du nombre de spins de 5%, mesuré par la R.P.E. est significatif? Cette écart me parait tomber dans la limite de précision de mesure. C'est au moins l'opinion de la plupart des chercheurs utilisant cette technique.

M. Nechtschein (*Grenoble, France*): Il est vrai que cet écart de 5% est de l'ordre de grandeur de l'incertitude sur l'évaluation du nombre de spins libres par RPE. Cependant nous avons effectué nos mesures sur 10 échantillons. Les écarts quadratiques moyens montrent qu'il s'agit de deux populations méres différentes (J. Gallard, M. Nechtschein, M. Soutif, et Ph. Traynard, *Bull. Soc. Chim. Fr.*, sous presse).

J. Josefowicz (*Ecole de Physique et Chimie, Paris, France*): Vous avez mentionné dans votre exposé des determinations de RPE et de pouvoir catalytique effectuées sur des ≪noirs d'aniline≫. Il découle de l'étude que nous avons entreprise et des données publiées sur ces materiaux, que ceux-ci constituent une classe de composés dont la structure, d'ailleurs mal connue, varie profondement selon les conditions de preparation. Dans ces conditions, je suis surpris de constater que vous décrivez les propriétés de RPE et de pouvoir catalytique par une seule valeur numerique; ceci d'àutant plus que les données publiées sur la conductivité aussi que nos premiers resultats montrent une variation de celle-ci étalée sur plusieurs ordres de grandeur.

J. Gallard: Nous n'avons pas tenté de montrer une corrélation entre activité catalytique et structure du noir aniline. Nous avons verifié sur plusieurs échantillons de noir d'aniline que la RPE donnait un signal reproductible.

D'autre part, nous n'avons jamais considéré de parallelisme entre activité catalytique et semi-conductivité. Nous ne supposons pas à priori qu'il existe une rélation entre semi-conductivité et spins libres dans les polyméres conjugués.

R. Buvet (*Ecole de Physique et Chimie, Paris, France*): Les produits oligoméres d'oxydation de l'aniline peuvent différer les uns des autres selon les conditions de préparation par: (*1*) le degré de polymérisation; (*2*) les positions relatives sur chaque cycle des atomes d'azote servant à l'enchaînement; (*3*) le degré d'oxydation pour un squelette donné; (*4*) le degré de fixation de protons, lié au caractére acide-base; (*5*) et éventuellement la formation de complexes avec des cations etrangers. Si les chiffres que vous avez présentés, correspondent à des conditions de préparation ou de traitement differentes, il faudrait déduire de la comparaison des mesures effectuées au laboratoire et des votres qu'alors que ces variations de composition retentissent profondément sur la mesure de conductivité, elles n'ont que peu d'effet sur les mesures de RPE et de pouvoir catalytique. Ceci me semble difficile à retenir étant donné les trés importantes variations possibles de composition, en particulier celles liées à l'oxydoréduction de ces composés.

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Modification of Electronic Properties of Some Synthetic Polymers

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It was stated in a previous paper[1] that vinyl polymers irradiated with ultraviolet light of suitable wavelength exhibit electronic properties changes. In the case of vinyl chloride copolymers with vinylidene chloride a decrease of surface and cross-sectional specific resistance and the photoconductivity were observed.

Vinyl polymers are known to exhibit electric resistance changes when pure samples or samples with metallic ions are pyrolyzed[2] or fine metal powders are introduced.[3]

In this paper we shall report on the effect of introducing metal ions and semiconducting compounds into vinyl polymers on the electric conductivity and photoconductivity of the polymers.

EXPERIMENTAL

Characteristics of the Materials Studied

In our studies we used two kinds of polymers: (a) those which do not degrade markedly under irradiation by ultraviolet light and (b) those which can be modified by ultraviolet irradiation, giving conjugated systems like vinyl chloride and its copolymers with vinylidene chloride.

Polystyrene was obtained by the bulk thermal polymerization of twice-distilled monomer, flushed and sealed under nitrogen. The temperature of the bath was 125°C. The polymer was purified by dissolving in benzene and precipitated with excess methyl alcohol. The solid polymer was filtered and dried in vacuum at 105°C.

Polyvinyl chloride (PVC) was a commercial product which was twice purified by dissolving in cyclohexanone, precipitated with methyl alcohol, and dried in vacuum at 55°C. after washing with acetone.

Copolymers of vinyl chloride with vinylidene chloride were commercial products which were purified by dissolving in DMF, precipitated with water and acetone, and then dried in vacuum at 55°C.

Semiconducting sulfides (ZnS, CdS) were obtained from analytically pure salts by precipitation with H_2S from aqueous solution by classical methods of inorganic chemistry. The precipitates are colored or white voluminous powders. After washing with H_2O they were dried to constant weight.

Some sulfides samples used were treated with activating salts and heated at a temperature of 900°C. In order to obtain pure semiconducting compounds with known amount of different ions, the activating salts $Cu(NO_3)_2 \cdot 3H_2O$ and $CdCl_2$ were added without generally used fusing agent. Mixtures of ZnS with activator were dried at 100°C. and heated in the oven in the same manner as sulfides without activators. In order to prevent oxidation ZnS on heating in the oven, a small amount of pure sulfur was added.

Preparation of Polymer Films Containing Metal Ions or Semiconducting Compounds

Films of vinyl chloride copolymer with vinylidene chloride were used as they are produced by Dow Co. (Saran B). The films of polyvinyl chloride were obtained by casting from solutions in dioxane. The use of a rather viscous solution prevents the cast from running or spreading over the casting surface.

The films of polystyrene were obtained from solutions in benzene or by melt pressing of solid polymer between two sheets of aluminum foil. The thickness of the films was about 0.01 mm.

The metal salts (ions) were introduced into polymer films by swelling saran or PVC films in mixtures containing tetrahydrofuran or dioxane (20 ml.) and saturated aqueous solutions of Zn and Cd salts (5 ml.).

The appropriate amount of aqueous salt solution prevents the dissolution of these polymer films and permits only their swelling.

Thorough washing off of the ions adsorbed on the surface is of great importance in investigations of electric properties. First acetone, which dissolved the solvents, was used for extraction; in the last stages of film washing water was used and, before drying in vacuum, the water was removed by a short immersion in acetone.

Most frequently metals were introduced into swollen polymer films in the form of chlorides in order to enable at the end of the extraction the control of the lack of Cl^- in the solvent.

The metal salts were introduced into swollen, previously irradiated or nonirradiated films. Irradiation yields partial crosslinking and so causes a decrease in the swelling and metal ions absorption ability.

The treated films were subsequently irradiated with ultraviolet light, low pressure and medium pressure mercury lamps being used as sources. Semiconducting compounds such as ZnS were introduced into polymer films in two ways: (a) the films were cast from suitable rather highly concentrated solutions containing an appropriate amount of ZnS or CdS powder, and in some cases the films were obtained by pressing; (b) the films containing metal salts were treated with H_2S in order to obtain metal sulfides. As the film thickness is rather small and the diffusion of H_2S into degassed films is fast, one week's storage of films in H_2S atmosphere seems to be sufficient for this aim.

In some cases the metal sulfides were obtained forth by immersing the films in a mixture of dioxane and aqueous Na_2S solution. At a suitable mixture composition the formation of sulfides proceeds rapidly.

The introduction of Zn or Cd salts from solutions into polystyrene films is very difficult. This is due to the fact that polystyrene films can be swollen in solvents which do not form homogeneous mixtures with water–salt solutions. Thus, polystyrene films containing ZnS or CdS were obtained by casting of polystyrene–benzene solutions with appropriate amounts of the above-mentioned crystalline powders.

The precise determination of the content of Zn and Cd ions introduced by swelling in saran and PVC films is very difficult. On the basis of polarographic determinations this content was estimated at about 1.5% after 2 hr. swelling and about 3% after 24 hr.

Most experiments were carried out with Zn ions or ZnS-containing films. The films with Cd ions and CdS were studied less systematically.

Films containing metal sulfides are opaque, so that their absorption spectra can not be investigated.

The method of irradiation of the above-mentioned films is the same as in the case of pure films and films containing metal salts.

The low pressure mercury lamp gives mainly radiant energy at the mercury line (254 mμ). The energy output of this lamp was not exactly determined. In all exposures the films were placed 10 cm. from the surface of the lamp. The preservation of these conditions permitted a relative qualitative comparison of radiation effects.

Near and far ultraviolet light was obtained from a Phillips HPW 125-w. mercury lamp with known spectral distribution. The samples were always kept at same 15 cm. distance in the irradiation experiments and the photoconductivity studies.

Electrical Measurements

Electrical resistance was determined with a specially constructed micromicroammeter of sensitivity 10^{-13} A. The work of this instrument is based on two electrometric valves in a bridge system with a subsequent amplification. The variable power supply extends from 0 to 500 v., so resistances up to 10^{16} ohms can be determined.

Electrical contact of samples was assured by use of a conducting paint (Silpaint No. 340, Hardy & Harman). In the present work the surface resistance was measured, and the electrodes were placed on both ends of investigated sample. The measurements were carried out at room temperature at constant humidity conditions. As all measurements were carried out at the same temperature and conditions and as the aim of this paper is to study the influence of metal ions or semiconducting compounds on the resistance and photoconductivity of specimens, the influence of electrodes will not be discussed in detail. In photoconductivity studies the electrodes were not irradiated with ultraviolet light.

RESULTS AND DISCUSSION

Absorption Spectra of Ultraviolet-Irradiated Films Containing Absorbed Metal Salts

Nonirradiated saran and PVC films and those without metal salts exhibit small absorption in visible light and in ultraviolet up to 2500 A. Films subjected to ultraviolet irradiation undergo modification, and their light absorption changes, showing a diffuse maximum at 275 mμ with a longtail going up to the visible region.[1]

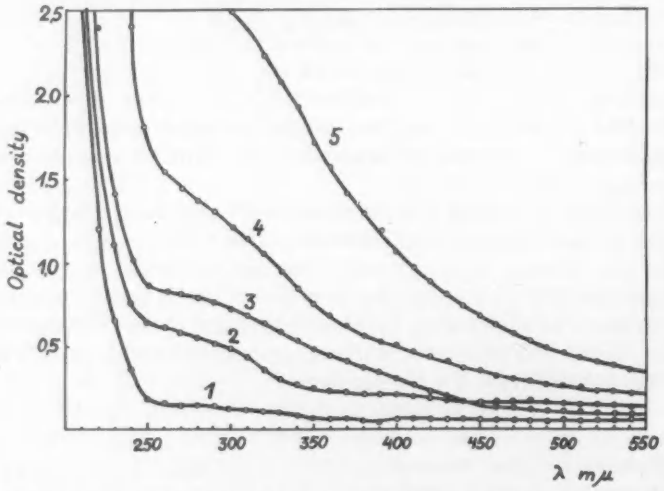

Fig. 1. Absorption spectra of Saran films containing $ZnCl_2$: (*1*) nonirradiated pure film; (*2*) film with $ZnCl_2$, dried at 65°C. for 2 hr. in vacuum; (*3*) the same film as in point 2 after ultraviolet irradiation (254 mμ) for 2 hr.; (*4*) film with higher $ZnCl_2$ concentration dried as in (*2*); (*5*) film as in (*4*) after ultraviolet irradiation (254 mμ) for 2 hr.

Small amounts of $ZnCl_2$ and $CdCl_2$ introduced into the films dried in vacuum at room temperature do not change the absorption spectra of the films. On the contrary, when these films are dried in vacuum at 65°C. their absorption spectra change significantly, depending on the content of metal salts and the drying time.

From the similarity of the character of absorption curves *2* and *3* on Figure 1, to the absorption curves of pure irradiated films, it can be suggested that the mechanisms of processes in both cases (irradiation and heating in presence of $ZnCl_2$) are similar.

The samples with $ZnCl_2$ dried at 100°C. in vacuum show an accelerated degradation (pure films heat-treated at 100°C. do not change their light absorption). Their absorption spectra (Fig. 2) are slightly different from those presented on Figure 1.

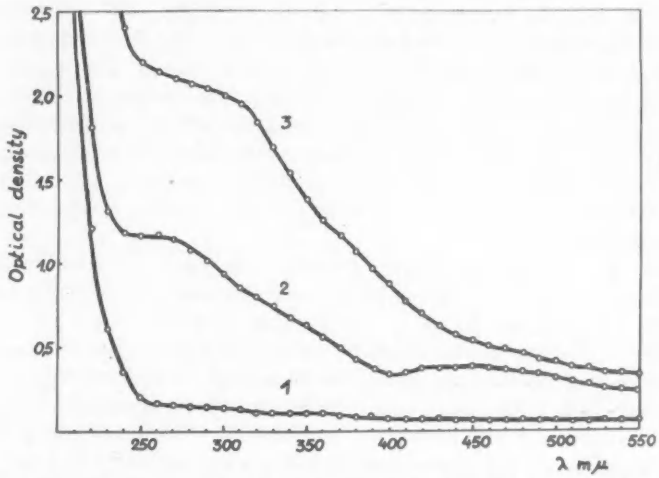

Fig. 2. Absorption spectra of Saran film containing $ZnCl_2$: (*1*) nonirradiated pure film; (*2*) film with $ZnCl_2$, dried at 100°C. for 2 hr. in vacuum; (*3*) the same film as in (*2*) after ultraviolet irradiation (254 mμ) for 2 hr.

The short wavelength maximum is shifted towards shorter λ and the second diffuse maximum appears at $\lambda \sim 450$ mμ. Subsequent irradiation of the same samples with a low pressure mercury lamp causes rather marked increase in absorption.

As the general character of absorption spectra of PVC films with and without $ZnCl_2$, both nonirradiated and irradiated, is rather similar to that of saran films we don't present these diagrams.

The degradation of Saran and PVC was discussed by several authors[4–7] and observed processes were explained by splitting off of HCl leaving behind double bonds. According to the so-called allylic chlorine concept, the dehydrochlorination proceeds along the chain creating by the "zippering effect" a long sequence of alternating single and double bonds. The HCl removed from the degrading molecule should act as accelerator. Winkler[8] stated that the conjugation of double bonds would tend to stabilize rather than to activate the allylic carbon, thus questioning the importance of the zippering theory and suggested that dehydrochlorination is a free radical reaction.

When Zn and Cd stabilizers were used, much less discoloration in the early stages of heating and irradiation was observed. With longer time of irradiation (or heating), the deterioration was rapid, and dark specimens were obtained. It was suggested that, when Zn soaps are used as stabilizers, $ZnCl_2$ or $HZnCl_2$ is formed during the degradation. These compounds catalyze the degradation.

In our samples irradiated or heated in air oxidation took place. The products of oxidation in which there are conjugated double bond systems

and free radicals, are responsible for discoloration. The existence of carbonyl groups produced in chlorine-containing vinyl polymers in presence of Zn and Cd salts was first suggested by Fuchsman.[9] The mechanism of oxidation with molecular oxygen is probably a free radical mechanism.

According to the data of Druesdow and Gibbs[10] not all oxidation intensifies the color. According to Fuchsman's theory the removal of HCl involving neighboring carbon atoms of polymer molecule (para-dehydrochlorination) and not neighboring carbon atoms (dia-dehydrochlorination) can take place.

However Zn and Cd soaps favor the dia-dehydrochlorination with production of tertiary and quaternary carbons and provide limits to the length of conjugated double bonds systems; $ZnCl_2$ does not act in this manner. The films containing these salts show a faster discoloration and the number of C=C bonds created by ultraviolet irradiation or heat does not diminish so rather a decrease in resistance can be expected. This was seen in comparison with pure films (see Table I). The crosslinking occurring in irradiated films causes considerable internal stresses which can lead to breaking of bonds with creation of two free radicals. These may undergo oxidation or, in the proposed dia-dehydrochlorination, may be stable. This may also be a reason for creation of "loose" electrons which enhance the conductivity.

This occurs both in films containing $ZnCl_2$ and pure irradiated films. The third factor which favors the larger conjugation is the possibility of formation of a six-membered ring through dia-dehydrochlorination. A spiral formation with five carbons per coil can exist without any appreciable strain. Further cleavage of the ring at the site of the dehydrochlorination would result in associated olefinic linkages in conjugation with carbonyl groups. This leads to intense discoloration and to a greater number of loose electrons.

Under the conditions of irradiation of the present study, the polystyrene films exhibit only a very slight yellow discoloration. A relatively broad absorption in polystyrene films which is concentrated at about 3400 A. is associated with a partial carbonization. The carbonization is primarily due to the formation of carbon-carbon bonds between atoms in adjacent benzene rings.

Electrical Properties

a. Surface Resistance. This work concerns mainly the surface resistance and photoconductivity. Most measurements were carried out on Saran and PVC films. As mentioned above, the polystyrene films hardly absorb metal salts and ZnS is hardly formed in them under the action of H_2S.

The results of surface resistance and photoconductivity measurements are gathered in Tables I–V.

Some experiments were carried out on Saran Samples irradiated before swelling.

For instance, a sample irradiated for 2 hr. with ultraviolet light of $\lambda \sim 254$ mμ gave about 15% of gel fraction as a result of crosslinking. The sample was then swollen for 3 hr. in the above-mentioned $ZnCl_2$ solution. After 2 hr. drying in vacuum at 65°C. the surface resistance of the sample (300 mm.^{2}) was $2 \times 10^9\Omega$. The same sample irradiated subsequently for 1 hr. with the HPW lamp showed a decrease of resistance to $7.1 \times 10^8\Omega$.

TABLE I
Surface Resistance of Saran B Films (300 mm.^{2}) Containing $ZnCl_2$

	Sample treatment						
		Drying in vacuum					
Sample no.	Swelling time, hr.	Time, hr.	Temp., °C.	Irradiation time, hr. (and type)	Surface resistance, ohms	Ohm's law[a]	Photoconductivity[b]
1		Pure film		—	3×10^{15}	+	0
2		Pure film		24 (254 mμ)	4×10^{12}	0	+
3	2	2	65	—	2.3×10^{13}	+	
4	4	2	65	—	1.1×10^{13}	+	0
5	22	2	65	—	7.0×10^{12}	+	0
6	4	2	100	—	1.6×10^{10}	+	0
7	4	4	100	—	6.2×10^{9}	+	0
8	4	2	65	0.25 (254 mμ)	1.1×10^{11}	0	0
9	3.5	2	100	2 (254 mμ)	2.5×10^{8}	0	0
10	22	2	100	2 (254 mμ)	3.1×10^{8}	0	0
11	5	2	65	4 (254 mμ)	5×10^{9}	0	0
12	2	2	65	15 (254 mμ)	1.1×10^{9}	0	0
13	2	2	65	1 (HPW)	6.2×10^{8}	0	0
14	18	2	65	1 (HPW)	1.2×10^{8}	0	0

[a] Here + signifies that Ohm's law is followed over the studied voltage region of 5–500 v.; 0 signifies that Ohm's law is not followed.

[b] Here + and 0 denote, respectively, the existence or lack of photoconductivity; ++ signifies very marked photoconductivity present.

Some experiments were carried out in order to test the effect of simultaneous ultraviolet irradiation. Saran film (300 mm.^{2}) immersed in solution of $ZnCl_2$ + water + tetrahydrofuran irradiated directly with low pressure mercury lamp gave a sample which, after drying for 2 hr. at 65°C. in vacuum and subsequent irradiation for 2 hr. with the same lamp, showed a surface resistance of $2 \times 10^8\Omega$. In the case of similarly prepared sample irradiated for 24 hr. after drying, the surface resistance was $5 \times 10^7\Omega$.

TABLE II
Time Dependence of Surface Resistance for Saran Samples (300 mm.²) Containing $ZnCl_2$

Sample 11[a]		Sample 12[a]	
Time, hr.	Surface resistance, ohms	Time, hr.	Surface resistance, ohms
0	5.9×10^9	0	1.1×10^9
1	6.3×10^9	1	1.1×10^9
15.5	1.0×10^{10}	16.5	6.8×10^9
19.5	1.25×10^{10}	24.0	1.2×10^{10}
21.5	1.31×10^{10}	39.0	5.6×10^{10}
25.5	1.78×10^{10}	44.0	1.2×10^{10}
39.5	1.78×10^{10}	58.0	1.2×10^{11}
43.5	2.00×10^{10}	62.0	1.1×10^{11}
44.5	2.00×10^{10}	68.0	1.2×10^{11}
64.5	2.00×10^{10}		

[a] Preparation conditions and irradiation time for these samples are given in Table I.

TABLE III
Surface Resistance and Photoconductivity of PVC Films (300 mm.²) Containing $ZnCl_2$

	Sample treatment						
		Drying in vacuum					
Sample no.	Swelling time, hr.	Time, hr.	Temp., °C.	Irradiation time, hr. (and type)	Surface resistance, ohms	Ohm's law[a]	Photoconductivity[b]
1	Pure film			—	4.5×10^{14}	+	0
2	Pure film			22 (254 mμ)	1.5×10^{13}	+	+
3	2	2	65	—	7.5×10^{13}	+	0
4	4	2	65	—	4.8×10^{13}	+	0
5	22	2	65	—	2.0×10^{13}	+	0
6	4	2	100	—	2.0×10^{13}	+	0
7	4	4	100	—	5.2×10^{12}	+	0
8	4	2	65	2 (254 mμ)	4.8×10^{12}	0	0
9	4	2	65	22 (254 mμ)	2.1×10^{11}	0	0
10	4	2	100	2 (254 mμ)	2.1×10^{11}	0	0
11	4	4	100	2 (254 mμ)	7.8×10^{10}	0	0
12	2	2	65	2 (HPW)	3.8×10^{10}	0	0
13	4	2	100	2 (HPW)	9.0×10^9	0	0

[a,b] See Table I footnotes.

These experiments show that the degradative action of Zn^{++} ions in solution is more pronounced with simultaneous irradiation. The samples prepared in this way did not exhibit the photoconductivity.

The changes of the surface resistance with time were studied, in order to get some indications of the ionic part of surface conductivity. The results obtained for two samples are given in Table II.

From the data of Table II it can be seen that the surface resistance achieved a more or less constant value after two days. The changes relating to the initial value are rather great.

The conductivity of films after this period is associated with permanent changes of structure due to the presence of Zn^{++} ions and ultraviolet irradiation.

The results of measurements of surface resistance of PVC 300 mm.^{2} films containing $ZnCl_2$ are given in Table III.

The change in surface resistance of PVC films with time is similar to that of saran. After two days a constant resistance is obtained.

Further measurements related to the surface resistance and photoconductivity of films containing ZnS (Table IV). There were no or small changes of surface resistance in comparison with values found for ultraviolet irradiated pure Saran films. The films with ZnS exhibit photoconductivity, unlike those containing $ZnCl_2$.

Some experiments were carried out with $CdCl_2$ and cadmium sulfides. The results are gathered in Table V.

The investigations of ultraviolet and visible light absorption spectra showed an accelerated degradation of vinyl polymers in the presence of Zn ions. Similar results were obtained with Cd ions introduced into investigated polymers. Neither salt used ($ZnCl_2$ and $CdCl_2$) acts as an HCl acceptor or an oxidation catalyst. These salts are also not free radical scavengers because of their existence in the single valence state. Thus, the degradation results in formations of groups and species which cause the decrease of resistance. Even taking into consideration the ionic part of conductivity (Zn^{++} and absorbed HCl) it was found that the decrease of resistance (Tables I–III) is due to a change in structure of the investigated materials. As noted above, it is difficult to say more about the kind of chemical structures in which Zn or Cd atoms take part. It is not excluded that these atoms are built into the polymer chains (in these parts where H atoms are detached). They could also form intramolecular bonds in higher steps of degradation processes.

The degradation process is much less influenced by ZnS or CdS. The resistance values of irradiated Saran and PVC containing these sulfides are not much different from these of pure irradiated films.

The saran and PVC films containing $ZnCl_2$ and ZnS (crystalline and amorphous) showed current changes with applied voltage following Ohm's law unlike those which were subsequently irradiated.

The high resistance and small effects of photoconductivity observed in polystyrene films containing ZnS–Cu or ZnS–Cd suggest that the poly-

TABLE IV
Surface Resistance and Photoconductivity of Vinyl Polymer Films Containing ZnS

Sample no.	Sample type	Sample treatment: Swelling time, hr.	Drying in vacuum: Time, hr.	Drying in vacuum: Temp., °C.	ZnS content and preparation	Irradiation time, hr. (and type)	Surface resistance, ohms	Ohm's law[a]	Photoconductivity[b]
1	Saran	4	2	65	>1.5%; H_2S	—	1.5×10^{15}	+	0
2	Saran	22	2	65	~3%; H_2S	—	9.6×10^{14}	+	0
3	Saran	22	2	65	~3%; Na_2S	—	9.8×10^{14}	+	0
4	Saran	4	2	65	>1.5%; H_2S	24 (254 mμ)	8.5×10^{12}	0	+
5	Saran	2.2	2	65	~3%; H_2S	24 (254 mμ)			
6	Saran	22	2	65	~3%; H_2S	4 (HPW)	4.6×10^{12}	0	+
							4.2×10^{12}	0	+
7	Saran	—	—	—	Crystalline, 5%	—	4.2×10^{14}	+	+
8	Saran	—	—	—	"	24 (254 mμ)	6.8×10^{11}	0	++
9	Saran	—	—	—	Crystalline, 5%; ZnS + Cu	—	2.8×10^{14}	+	+
10	Saran	—	—	—	"	24 (254 mμ)	2.8×10^{11}	0	++
11	Saran	—	—	—	"	2 (HPW)	3.2×10^{11}	0	++
12	PVC	4	2	65	>1.5%; H_2S	—	1.3×10^{14}	+	0
13	PVC	22	2	65	~3%; H_2S	—	0.5×10^{14}	+	0
14	PVC	4	2	65	~1.5%; H_2S	24 (254 mμ)	9.1×10^{12}	0	+
15	PVC	22	6	65	~3%; H_2S	24 (254 mμ)	3.7×10^{12}	0	+

16	PVC	22	6	65	~3%; H_2S	4 (HPW)	1.9×10^{12}	0	+
17	PVC	—	—	—	Crystalline, 5%	—	9.3×10^{14}	+	+
18	PVC	—	—	—	Crystalline, 5%	22 (254 mμ)	3.0×10^{12}	0	++
19	PVC	—	—	—	"	2 (HPW)	9.1×10^{11}	0	++
20	PVC	—	—	—	Crystalline, 5%; ZnS + Cu	—	7.5×10^{13}	+	+
21	PVC	—	—	—	"	22 (254 mμ)	$5.8 + 10^{11}$	0	++
22	PVC	—	—	—	"	2 (HPW)	6.3×10^{11}	0	++
23	PS[c]	—	—	—	Crystalline, 5%	—	6.8×10^{15}	0	+
24	PS	—	—	—	"	22 (254 mμ)	5.2×10^{15}	0	+
25	PS	—	—	—	"	2 (HPW)	3.4×10^{15}	0	+
26	PS	—	—	—	Crystalline, 5%; ZnS + Cu	—	2.1×10^{15}	+	+
27	PS	—	—	—	"	22 (254 mμ)	2.7×10^{15}	0	+
28	PS	—	—	—	"	2 (HPW)	2.0×10^{15}	0	+

[a,b] See Table I footnotes.

[c] Polystyrene.

TABLE V
Surface Resistance and Photoconductivity of Vinyl Polymer Films Containing CdS

Sample no.	Sample type	Sample treatment: Swelling time, hr.	Sample treatment: Drying in vacuum, Time, hr.	Sample treatment: Drying in vacuum, Temp., °C.	CdS content and preparation	Irradiation time, hr. (and type)	Surface resistance, ohms	Ohm's law[a]	Photoconductivity[b]
1	Saran	24	2	65	~3.0%; H_2S	—	1.3×10^{15}	+	0
2	Saran	22	2	65	"	24 (254 mμ)	9.6×10^{12}	0	+
3	Saran	22	2	65	"	4 (HPW)	8.2×10^{12}	0	+
4	Saran	—	—	—	Crystalline, 5%	—	2.6×10^{15}	+	+
5	Saran	—	—	—	"	24 (254 mμ)	3.6×10^{12}	0	++
6	PVC	22	2	65	~3%; H_2S	—	6×10^{14}	+	0
7	PVC	22	2	65	"	24 (254 mμ)	2.4×10^{12}	0	+
8	PVC	—	—	—	Crystalline, 5%	—	8.1×10^{14}	+	+
9	PVC	—	—	—	"	24 (254 mμ)	3.6×10^{12}	0	+
10	PS	—	—	—	"	—	6.2×10^{15}	0	+
11	PS	—	—	—	"	24 (254 mμ)	4.0×10^{15}	0	+

[a,b] See Table I footnotes.

meric material (taking into consideration the low amount of semiconducting compounds) which hardly changes its structure on ultraviolet irradiation acts as a good insulator.

All experiments discussed in this paper were carried out for such periods of ultraviolet irradiation which permitted the investigation of ultraviolet and visible light absorption spectra. At higher doses the irradiated saran and PVC films containing $ZnCl_2$ and $CdCl_2$ became black. The results of a study of electronic properties of films prepared in this manner will be reported in a future publication.

The introduction of Zn and Cd salts, their subsequent transformation into sulfides, and ultraviolet irradiation permit the electronic properties of chlorine-containing vinyl polymers to be varied to different controlled degrees.

Photoconductivity. The aim of this study was to investigate the influence of Zn^{++} and ZnS or activated ZnS–Cu on the electronic properties of ultraviolet-irradiated and unirradiated vinyl polymer films. Thus, the absolute photoconductivity gain $G = \Delta I/eF$, where ΔI is the induced electric current, F is the number of photons absorbed per unit of time, and e is the electron charge, is not given. The results of these investigations will be published later. The unirradiated Saran and PVC films containing Zn^{++} or Zn in form of different amorphous compounds do not exhibit photoconductivity; however, these ions and/or compounds accelerate the decomposition and cause the resistance decrease.

In all our experiments the concentration of semiconducting compounds was low. It seems to be justified to assume that the grains of semiconducting fillers were sufficiently separated from each other and that the change of electronic properties (e.g., photoconductivity) occurs with large participation of the polymer medium.

It can be seen from Table IV that the photoconductivity exists mainly in samples containing crystalline ZnS. This shows that, as presumed, the amorphous ZnS formed in the films slightly influences the photoconductivity.

In this case, the observed photoconductivity should be related to the ultraviolet modification of polymeric material between the grains of amorphous ZnS. It can be supposed that HCl evolution during irradiation has only a slight influence on the ZnS produced in the films. Even the Cl^- on the surface of ZnS grains could be considered only to be an activator which does not, however, change the amorphous characteristic of inorganic fillers.

In the case of pure crystalline ZnS and CdS the increase of photoconductivity is not very remarkable in comparison with that of the pure irradiated films. This could be attributed to the deficiency of larger amount of localized charge. The deficiency of S ions (faster evaporation of S by roast-sintering) and the related excess of Zn ions do not produce enough electrons which by light absorption could be transferred to the conduction band and could influence the π-electrons of conjugated double

bonds formed on the surface of the crystals in vinyl polymers by ultraviolet irradiation. Sulfide-containing films showed the photoconductivity effect on irradiation with light of longer wavelengths than in the case of pure, previously irradiated films.

This is probably due to the absorption of longer wavelengths by activator atoms. Only preliminary studies of the effect of wavelengths upon the photoconductivity of films containing ZnS–Cu or ZnS–Cd have been carried out. The result is that even light in the region of 4500–5500 A. causes a photoconductivity effect. Ultraviolet light is however more effective. This supports the idea that the photoconductivity is due to absorption in activator levels, which is consistent with the observed fluorescence spectrum of ZnS–Cu (blue) and ZnS–Cd (yellow). In these cases, the fluorescent light could also excite the photoconductivity of the samples. The existence of the phosphorescence of the films with ZnS–Cu and ZnS–Cd content corresponds to the longer decay time of photoconductivity in comparison with that for pure irradiated saran film samples.

The applied electric field also liberates the electrons from lower traps in ZnS–Cu than is possible by thermal activation, so the ZnS–Cu of crystals have a greater influence on the electronic properties of the investigated films.

c. Polarization. Many insulating photoconductive substances show electric polarization. This is assumed to be due to the immobility of positive charges and the trapping of electrons moving in the conduction band and/or to their eventual removal from the material by the electric field. These effects are an inherent interfering effect in the studies of photoconductivity. This polarization of different duration was studied by several authors for some electrets[11,12] crystals,[13] and crystalline powders introduced in insulators.[14] We found that similar effects exist in irradiated pure Saran films and especially in films containing ZnS. The nonirradiated films show this effect in much less pronounced manner. In irradiated pure films even a small number of displaced charges (perhaps in the form of trapped radicals) is sufficient for polarization.

In the case of samples containing semiconducting powders, the slight polarization in the nonirradiated samples is due to the fact that there is a small amount of free charge. This is also related to the phosphorescence in pure irradiated saran film and films containing phosphorescent semiconducting powders. Up to now no unified concept can be presented as to how the polarization is established. In films containing the semiconducting powders the polarization in the crystalline portion is associated with displacement of free electrons in the conduction band, while the positive charge is localized in activators. It is difficult to say whether the distribution of charges is homogeneous or inhomogeneous.

It seems that this does not influence significantly the general character of the phenomenon.

It is also possible that a sample placed immediately after irradiation in the electric field is no longer electrically neutral due to the charges

removed from or injected into the sample. This effect, as well as dipole alignment seems to be of minor importance. The determination of charge distribution especially by surface resistance measurements and even cross-sectional resistance measurements is very difficult in the case of thin films.

The polarization observed in an electric field can be interpreted as an escape of new electrons from the traps as consequence of the field action. At the first moment after the application of the field, the polarization is larger. Then, with time, as the number of electrons released decreases, the rate of increase of polarization is slowly diminished. The discharge of polarization may cause the creation of mobile charges by radiation. With ultraviolet irradiation this process is faster than with visible light. This is related to the much smaller visible light absorption and with the fact that practically each absorbed ultraviolet quantum creates a free electron which moves through the polarization field and compensates the existing polarization. The heat has the same destroying action. In the case of irradiated films without ZnS it destroys the trapped radicals. In the case of ZnS-containing films its action is associated mainly with liberation of trapped electrons.

The details of the studies of discharge rate as influenced by humidity will be reported in a future publication. Polarization over a longer period of time thus involves displacement of free charges and their subsequent localization in deep traps or excitation of molecules which produces trapped radicals. The samples containing ZnS in the films are more easily polarizable because the creation of free charges by the electric field is easier. These samples undergo faster depolarization if there are remaining free charges which move in the internal field. The substances like ZnS–Cu and ZnS–Cd cause a more permanent polarization but they show a faster decay of photocurrent and phosphorescence after the radiative excitation is removed.

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Synopsis

Changes in electronic properties of ultraviolet-irradiated chlorine-containing vinyl polymers (Saran and PVC) on addition of Zn and Cd ions and Zn and Cd sulfides were investigated. The Zn and Cd ions were introduced into polymer films by swelling in appropriate mixtures of solvent and aqueous salt solution. The sulfides were formed in the swollen films by diffusion of H_2S (amorphous sulfides) or introduced by casting or pressing of films from mixtures with crystalline ZnS or CdS. It was found that the Zn and Cd ions accelerate the ultraviolet degradation causing discoloration and a large decrease in resistance. The presence of these ions in the studied films yields the disappearance of photoconductivity found in pure irradiated films. The amorphous and crystalline sulfides influence the resistance only very slightly but enhance the photoconductivity of irradiated films, especially those containing crystalline semiconducting powders. Films containing ZnS showed a larger polarization than the pure irradiated films. Some experiments carried out with polystyrene suggest that these effects are not only related to the presence of small amount of semiconducting compounds, but to intrinsic changes in the polymeric materials during irradiation. Some suggestions are given in order to explain the observed phenomena.

Résumé

On a étudié le changement des propriétés électroniques de polymères vinyliques chlorés irradiés par U.V. (Saran et PVC) en présence d'ions Zn et Cd et leurs sulfures. On a introduit les ions Zn et Cd dans les films polymériques par gonflement dans des mélanges appropriés de solvant et de la solution aqueuse du sel. Les sulfures se forment dans les films gonflés par pénetration de H_2S (sulfures amorphes) ou introduits par moulage ou pressage de films à partir de mélanges avec du ZnS ou CdS cristallin. On a trouvé que les ions Zn et Cd accélèrant la dégradation par U.V., provoquant la décoloration et une forte diminution de la résistance. La présence de ces ions dans les films étudiés provoque la disparition de la photoconductivité constatée dans des films purs irradiés. Les sulfures amorphes et cristallins n'influencent pas beaucoup la résistance mais augmentent la photoconductivité des films irradiés spécialement avec les poudres crystallines semiconductrices. Les films contenant du ZnS montrent une plus grande polarisation que les films irradiés purs. Certaines expériences effectuées avec du polystyrène suggèrent que ces effets ne sont pas uniquement reliés à la présence d'une faible quantité de composés semiconducteurs mais aussi aux changements intrinsèques dans les matériaux polymériques pendant l'irradiation. On fait des suggestions en vue d'expliquer les phénomènes observés.

Zusammenfassung

Die Änderung der elektronischen Eigenschaften UV-bestrahlter chlorhältiger Vinylpolymerer (Saran und PVC) durch Zn- und Cd-Ionen und Zn- und Cd-Sulfid wurde untersucht. Die Zn- und Cd-Ionen wurden durch Quellung in geeigneten Mischungen aus Lösungsmittel und wassrigen Salzlösungen in die Filme eingeführt. Die Sulfide wurden entweder in den gequollenen Filmen durch Permeation mit H_2S hergestellt (amorphe Sulfide) oder durch Giessen oder Pressen von Filmen aus Mischungen mit kristallinem ZnS oder CdS eingeführt. Die Zn- und Cd-Ionen beschleunigen den zu Verfärbung und starker Abnahme des Widerstandes führenden UV-Abbau. Die in reinen bestrahlten Filmen festgestellte Photoleitfähigkeit verschwindet in Gegenwart dieser Ionen in den untersuchten Filmen. Die amorphen und kristallinen Sulfide beeinflussen zwar den Widerstand kaum, erhöhen jedoch die Photoleitfähigkeit der bestrahlten Filme, insbesondere bei Verwendung von kristallinen halbleitenden Pulvern. Die ZnS-hältigen Filme wiesen eine höhere Polarisation als die reinen bestrahlten Filme auf. Einige an Polystyrol durchgeführte Versuche weisen darauf hin, dass diese Effekte nicht nur mit der Anwesenheit kleiner Mengen halbleitender Verbindungen, sondern auch mit grundlegenden Veränderungen des Polymeren bei der Bestrahlung in Verbindung stehen. Es wird versucht, die beobachteten Erscheinungen zu erklären.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1417–1427

Relationship between Luminescence and Semiconducting Properties of Some Synthetic Polymers

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The semiconducting properties of synthetic polymers are related mainly to the existence of long conjugated bond systems, heteroatoms, trapped radicals etc. These systems undergo excitation by light absorption of appropriate wavelength, creating excited states. Thus, compounds containing such systems should exhibit fluorescence and phosphorescence.[1]

The phosphorescence of solid inorganic substances is well known and its mechanism is related to the existence of active centers. The duration of phosphorescence of organic compounds at room temperature is generally much shorter and often phosphorescence can not be observed independently of fluorescence. This occurs particularly in the case of polymers which, unlike anthracene and dyes, have not been well investigated in the form of monocrystals. They are partially amorphous bodies.

In this paper some results of luminescence and conductivity investigations of polyamides and vinyl copolymers are discussed. In addition, some remarks are given on the influence of ultraviolet irradiation on the effects of the luminescence and conductivity in these materials.

EXPERIMENTAL

A. Sample Preparation

1. Polyamides. The polymer was prepared from hexamethylenediamine adipic salt (66 salt) according to the methods described by Sorenson and Campbell[2] and Coffman et al.[3]

The investigated films were obtained from formic acid solutions and dried in appropriate conditions or from the melt. The films were carefully extracted with ether and dried at 80°C. The thickness of the films was about 20–100μ.

2. Copolymers of Vinylidene Chloride with Vinyl Chloride. The polymers were commercial products which were dissolved in tetrahydrofuran, precipitated with water and then with acetone, afterwards dried in vacuum at 65°C.

Some films of these copolymers were studied after soaking in acetone as they were supplied by Dow Chemical Company or were obtained by melt pressing. They were investigated directly after drying.

B. Ultraviolet Source and Ultraviolet Irradiation

A HPW Philips 125 w. lamp with stabilized power supply was used for irradiation as well as for fluorescence and phosphorescence studies. The spectral distribution was determined by a quartz spectrograph. The relative intensities of main lines of this lamp are shown in Figure 1.

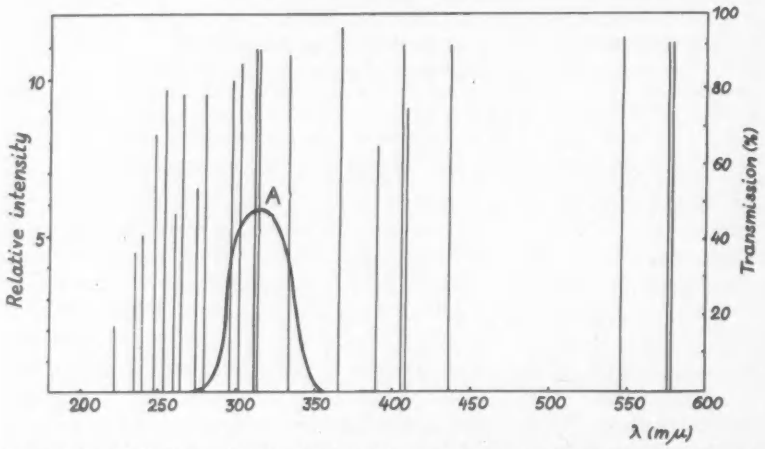

Fig. 1. The relative intensity of main lines of ultraviolet lamp. Spectral transmission of filter (A).

This lamp seems to be convenient for irradiation in these cases where no specific wavelength regions are required. It gives rather equal intensity distribution in near and far ultraviolet light. This permits the different wavelength regions of comparable intensity to be separated by using the appropriate filters. For studies of the effect of ultraviolet light on luminescence and conductivity no filters were used. The samples were kept 25 cm. from the ultraviolet light source and irradiated for different times in air at room temperature. Some experiments were carried out in vacuum in a quartz vessel.

For fluorescence studies a $NiCl_2$ solution filter together with a Wood filter was used. The spectral transmission of such a combined filter is also given on Figure 1.

The fluorescence spectra were taken with a quartz spectrograph of high luminosity. For fluorescence studies a special specimen holder was used which permitted the samples to be investigated at different angles. The fluorescence spectra were taken at 45° to the incident ultraviolet beam in order to diminish the registration of exciting reflected light. The incident ultraviolet beam after passing through the film went out through the window in the holder and was extinguished in a dark corner. The fluorescence intensity is dependent upon the surface roughness of the specimen, the flatness of the film, and the absorption characteristics of the film. The Ra-

man scattering is not of great importance because the fluorescence was studied mainly in the visible and near ultraviolet regions. Rayleigh scattering of the same wavelength as the exciting radiation interferes with the emission spectrum, but it occurs only in the near ultraviolet region, which in the present study is of less importance.

The relative intensity of fluorescence was determined by a recording microphotometer.

The phosphorescence was investigated in the same manner but with use of a mechanical phosphoroscope in order to eliminate the fluorescence.

The duration of polyamide phosphorescence was measured with a stop watch. In the case of polyvinylidene chloride copolymers, the short duration phosphorescence at room temperature was estimated from the speed of mechanical phosphoroscope.

C. Electrical Measurements

Electrical resistance was determined with suitable ammeter. The method of measurement was described in a previous paper.[4]

All resistance measurements were carried out at 65% R. H.

RESULTS AND DISCUSSION

A. Polyamides

1. Luminescence. The investigated polyamide sample (nylon 66) showed fluorescence and phosphorescence. A rather broad fluorescence spectrum of nylon 66 is localized in the near ultraviolet and in the visible region. The phosphorescence spectrum is shifted towards longer wavelengths. The phosphorescence duration of nonirradiated samples depends upon the irradiation time applied to excite the sample. The results of these investi-

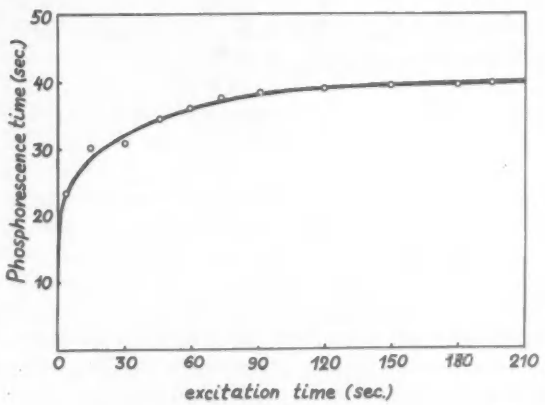

Fig. 2. The duration of phosphorescence as a function of excitation time (for not previously irradiated polyamide samples).

gations are given in Figure 2. It can be seen that after 2 min. irradiation the duration of phosphorescence is independent of the excitation time.

Other experiments were carried out on films previously irradiated with ultraviolet light. The studies were carried on in order to determine the influence of ultraviolet irradiation on the luminescence and the electric properties of polyamides. The irradiation time in these cases was much longer than the 3-min. period applied in previous phosphorescence studies carried out on the same samples.

If during modification the films were irradiated in air with ultraviolet light for a long time, a new absorption band appeared. It was situated at about 2900 A. in accordance to the data given by Ford.[5] The increase of this absorption band with irradiation time became slower when the irradiation time exceeded 50 hr.

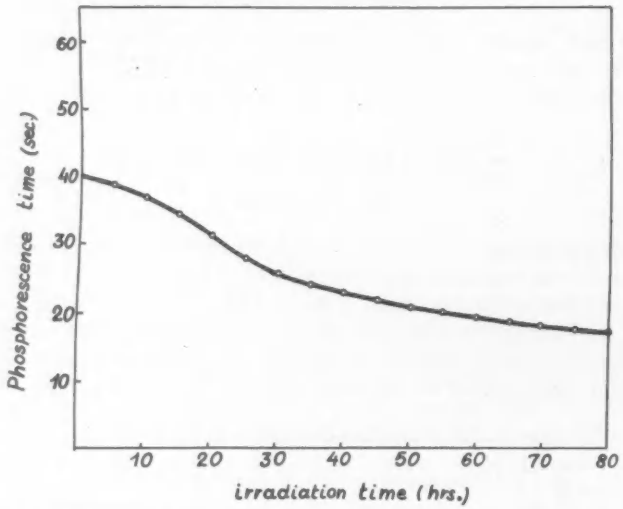

Fig. 3. The duration of phosphorescence vs. ultraviolet irradiation (modification) time for nylon 66.

For samples so irradiated the duration of phosphorescence decreased. The relation between the ultraviolet modification time and the phosphorescence time is presented in Figure 3.

A still faster increase of the above-mentioned absorption band was observed when the samples were kept in vacuum after previous irradiation in air (dark reaction). The absorption rise reached a maximum after about 12 hr. On reirradiation this band decreased to that value which was obtained during irradiation when the light was on.

These dark changes in the absorption band could not be related to the changes of the phosphorescence duration because each subsequent, even

short period of excitation with ultraviolet light caused a decrease of the absorption band. The phosphorescence time is thus the same as it would be without storing in dark.

These phenomena can be explained by the reactions which occur during the ultraviolet irradiation in air. The increase of the absorption band is connected with formation and subsequent oxidation of free radicals in polyamides. There is an equilibrium between the formation of peroxy radicals in air and their decomposition by ultraviolet irradiation. During the dark period free radicals are only oxidized by O_2 dissolved in the solid matrix. The absorption band is still increasing. When oxygen at the surface is used up, the slow diffusion of oxygen into the polymer is responsible for the slowing down of the increase of the absorption band.

When x-rays and other high energy radiation is employed, there are a large number of different ways in which the molecules may be broken up and various radicals formed.[6] It is usually very difficult to differentiate between them. In the case of ultraviolet irradiation the number of products is lower but it is also difficult to describe their exact chemical structure and to distinguish between them.

The same phenomena of oxidation of free radicals were observed for radical decay studied by electron spin resonance.[7,8]

It was also postulated that it is due to $\equiv C—O—O\cdot$ formation with subsequent formation of $HO_2^{\cdot}$ or similar species which react with nonradical products.

The same radical formation and oxidation phenomena show an influence on the phosphorescence duration.

The oxygen is known to be a quencher of phosphorescence even at small concentration. Thus, the formation of oxidized compounds is responsible for the decrease of phosphorescence. The observed phosphorescence is a surface phenomenon, so the radicals at (or very near) the surface act as centers of phosphorescence.

The oxygen molecules diffusing into solid polymer, become trapped in the vacancies and on the excited molecules and then interact with unpaired electrons of the polymer radicals localized close to the oxygen molecule.

It is of importance to consider the influence on the phosphorescence of the water absorbed at the surface of the studied films. Absorption of water has a slight annealing effect in nylon. Conditioning over water and then drying cause the increase of crystallinity somewhat 5%.[9] Work is in progress to elucidate this factor and now it can be said that H_2O decomposition products (by ultraviolet irradiation) react with radicals formed in the polyamide film, causing the decrease of phosphorescence ability.

2. Resistance. As the effects of irradiation and luminescence are surface phenomena, they may be connected with the surface resistance. The investigations of the surface resistance of irradiated polyamide films showed the relation between measured value and ultraviolet irradiation time. It should be remarked that the resistance changes of irradiated films are not so distinct as in the case of vinyl polymers containing chlorine atoms.

The relation between ultraviolet irradiation time and surface resistance is presented in Figure 4. The relation between the phosphorescence time and duration of ultraviolet irradiation is also given. The curves representing the decrease of resistance and the decrease of phosphorescence are similar in character, but the decrease of phosphorescence duration is connected with oxidation of radicals and the decrease of resistance of ultraviolet-irradiated samples is probably due to the breaking of hydrogen bonds between the polymer chains or between polymer chains and absorbed H_2O molecules. It seems that the discussed phenomenon is also influenced by the crosslinking and chain scission which occur on γ and high energy irradiations[10,11] as well as on irradiation with ultraviolet light.

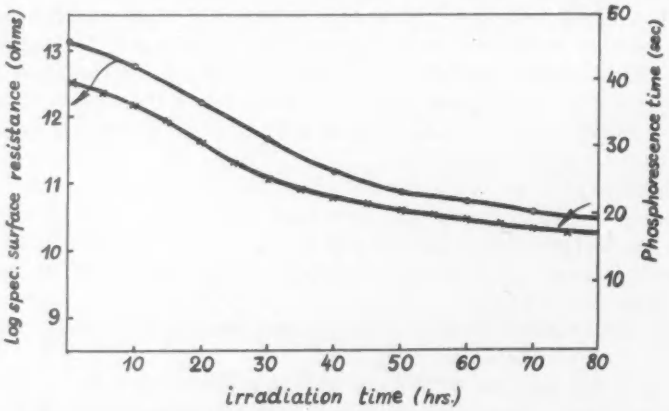

Fig. 4. The relation between ultraviolet irradiation time, specific surface resistance, and phosphorescence duration time.

The sorbed H_2O molecules are attached to the chains, even at rather high temperatures, strongly enough to move with the chains as they change configurations. They have a plasticizing action. The mechanism of conductivity in polyamides at low temperature is related[11,12] to the proton transfer, so breaking of the hydrogen bonds enhances the possibility of their rotation and facilitates the attainment of appropriate orientation in the amorphous regions in the electric field. It seems that the increase of the number of endgroups formed by the chain scission through ultraviolet irradiation is not the main factor which influences the decrease of resistance because a simultaneous crosslinking occurs. This is consistent with dielectric absorption studies.[10,11]

The breaking of some hydrogen bonds between segments of molecules is not the sole source of resistance decrease on irradiation. The isomerism of amide linkages proposed by Backer and Yager[13] for polyamides and first considered in the structure of polypeptides and proteins by Astbury[14] should be taken into consideration. These configurations which permit the

intermolecular hydrogen bonds may be regarded as virtually ionic.[15] The hydrogen atom in NH_2 may exist in two potential minima related to the oxygen of the adjacent chain and to its own nitrogen. The energy required for the hydrogen atom to oscillate is sufficiently supplied by ultraviolet quanta (it is at least comparable with N—H bond energy) and the ultraviolet quantum enables a translatory (vibratory) movement from the one potential minimum to the other in the dipole layers. Thus, the action of ultraviolet light is connected not only with rupture of hydrogen bonds between absorbed water and polyamide molecules but also with the evolving of H^+ from the nitrogen and oxygen atoms force fields.

The increase of mobility of chains in the amorphous regions should result also in the decrease of phosphorescence ability. It was found, however, that even in the case of long irradiation time the phosphorescence exists. Apparently the polycrystalline nature of polyamides presents coupling and entanglement effects which are more persistent than these in completely amorphous polymers. These cause the preservation of high local viscosity regions which prevent the thermal deactivation of excited states and the diffusion of oxygen.

B. Vinyl Copolymers (Copolymer of Vinylidene Chloride with Vinyl Chloride)

1. Luminescence. Some vinyl polymers show fluorescence when irradiated with ultraviolet light. In many cases described in the literature the observed fluorescence is due to impurities (mainly residual organic initiators).[16] In carefully purified samples the fluorescence is due to the double bonds which remain at the ends of the chains or are produced in the unavoidable degradation processes.

The investigated vinylidene chloride–vinyl chloride films irradiated with ultraviolet light exhibit fluorescence. This was already indicated in our previous paper.[17] When the polymer was carefully purified before film preparation, the fluorescence spectrum was localized in the near ultraviolet and visible region. The relative intensity distribution of this luminescence is shown in Figure 5. The curve is given only to 360 mμ because at the longer exposure which was necessary under our conditions to obtain the fluorescence spectrum (low intensity of emitted light) the scattered excitating light made it impossible to resolve the spectrum in the far ultraviolet region.

When this film was irradiated (modified) with ultraviolet light for several hours a new emission band appeared with a maximum at about 610 mμ (Fig. 5, curves *B* and *C*). This maximum increases with irradiation time but its position does not change.

The phosphorescence of vinylidene chloride–vinyl chloride films observed at room temperature is very weak. Even with long exposure times and with the use of a spectrograph of high luminosity it is difficult to record this spectrum.

The duration of the above-mentioned phosphorescence at room temperature is short. It is of the order of 10^{-2} sec. Studies of this phosphorescence at low temperature (liquid air) as well as these concerning monochromatic excitation are still in progress.

It seems that the observed luminescence phenomena are related to the vinylene chains and radicals produced in the films by ultraviolet irradiation. These undergo excitation by near ultraviolet light and cause the appearance of fluorescence and phosphorescence at longer wavelength than it was stated for unirradiated films.

It was found[17] that the long irradiation time does not yield a continuous increase of the length of conjugated bonds systems. This is consistent

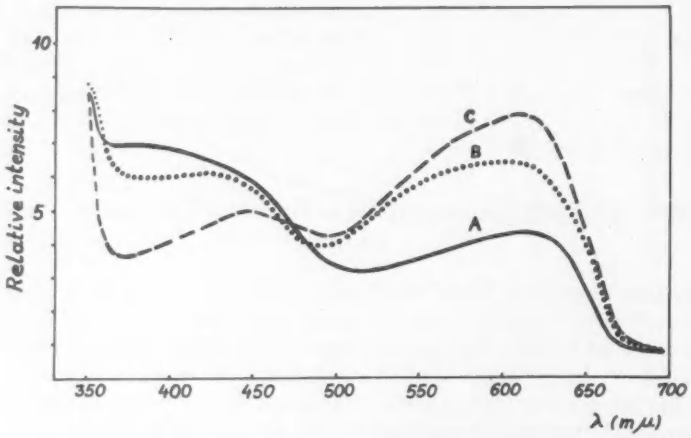

Fig. 5. The relative intensity distribution of fluorescence of nonirradiated and irradiated poly(vinylidene chloride–vinyl chloride) film: (*A*) nonirradiated film; (*B*) film irradiated with ultraviolet light for 2 hr.; (*C*) film irradiated with ultraviolet light for 6 hr.

with the observed fluorescence of irradiated films. The emission maximum of the films so irradiated does not shift towards longer wavelengths as ought to be observed in the case of the continuous increase of conjugation with time of ultraviolet irradiation. The free radicals being formed undergo oxidation, and it is possible that their existence does not interfere with the vinylene chains. As they are more easily oxidized than the vinylenes, their disappearance has a smaller effect on the luminescence.

2. Resistance. The irradiated films of vinylidene chloride–vinyl chloride copolymers show a decrease in surface resistance of the order of 10^2 or even more as was already described.[17] The decrease of conductivity is connected with the intensity increase of the fluorescence band.

A decrease in resistance of films irradiated in air is observed over a period of several hours of ultraviolet irradiation. The same behavior is found for

the increase of the new fluorescence band. The time in which the resistance decrease and fluorescence increase is observed is not only due to the filtering action of produced compounds but also to the oxidation phenomena which occur during longer periods of irradiation.

CONCLUSIONS

The luminescence of polyamides is related to the primary structures existing in nonirradiated films. They may be excited to the long-living excited states similar to those observed in polyamino acids or polyadenilic acid.[18]

In the vinyl copolymers discussed above the luminescence is due to the residual conjugated bonds.

The irradiation with ultraviolet light influences in a different way the luminescence phenomena and electrical resistance of two kinds of polymers mentioned above.

In polyamides the irradiation results in the decrease of duration of phosphorescence and in the decrease of resistance.

Another effect is observed in the chlorine-containing vinyl polymers. The irradiation causes formation of vinylene chains and so enhances the fluorescence ability and the shift of the fluorescence band towards longer wavelengths.

The resistance decrease simultaneously observed is mainly due to formation of vinylene chains, but crosslinking and ring formation must also be taken into account.

The existence of photoconductivity in vinylidene chloride–vinyl chloride copolymers was pointed out in a previous paper.[17] Photoconductivity is rather associated with free radicals or their reaction products with chlorinated conjugated structures; thus it is affected by oxidation. The fluorescence and phosphorescence is less influenced by the oxidation reaction. This is the reason for the faster decrease of photoconducting ability than of the luminescence ability.

The changes in the limited time of resistance as well as the constant position of the maximum of the fluorescence band are related to the determined length of conjugated systems and established structures formed by irradiation. A fast photoconductivity decay is difficult, however, to explain at the present state of investigations.

Thus the mechanism of luminescence and its relation to the electric properties in both polymers are different. It appears that the relations between the electric properties and luminescence changes (especially of phosphorescence) exist, and it seems that further studies of both phenomena will give some more indications about them and the excited states produced in polymers.

The authors wish to thank Dr. F. Boyer and Dr. Rector from Dow Chemical Company for samples they have kindly supplied.

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Synopsis

The luminescence (fluorescence and phosphorescence) and electrical resistance of polyamides and copolymers of vinylidene chloride with vinyl chloride as well as the influence of ultraviolet irradiation on both phenomena occurring in these polymers were investigated. It was found that ultraviolet irradiation influences in a different way the luminescence and resistance of both kinds of polymers. In polyamides, ultraviolet irradiation results in the decrease of duration of phosphorescence and resistance. The first phenomenon is due to the formation of radicals and their subsequent oxidation; the second is due to the breaking of intramolecular hydrogen bonds in the amorphous part of polymer, which enhances chains mobility and proton transfer by appropriate orientation of segments in electric field. The ultraviolet irradiation of vinyl polymers containing chlorine atoms causes formation of vinylene chains and results in greater luminescence ability and resistance decrease. The radicals being formed are more easily oxidized without change of vinylene sequences so the luminescence is not destroyed by the oxidation of radicals.

Résumé

On a étudié la luminescence, la fluorescence, la phosphorescence, ainsi que la résistance électrique de polyamides et de copolymères du chlorure de vinylidène et de chlorure de vinyle et l'influence de l'irradiation ultra-violette sur ces phénomènes dans ces polymères. On trouve que l'irradiation ultra-violette influence de différentes façons la luminescence et la résistance des deux espèces de polymères. Chez les polyamides, l'irradiation U-V provoque une diminution de la durée de phosphorescence et de la résistance. Le premier phénomène est dû à la formation de radicaux et à leur oxydation ultérieure, le second est dû à la scission de liens-hydrogène intramoléculaires dans la partie amorphe du polymère ce qui augmente la mobilité des chaînes et les transferts de protons par une orientation appropriée des segments dans un champ électrique. L'irradiation U-V des polymères vinyliques contenant des atomes de chlore provoque la forma-

tion de chaînes vinylène ainsi qu'une grande tendance à la luminescence alors que la résistance diminue. Les radicaux formés sont plus facilement oxydés sans changement des séquences vinylènes en sorte que la luminescence n'est pas détruite par l'effet d'oxydation des radicaux.

Zusammenfassung

Die Lumineszenz (Fluoreszenz und Phosphoreszenz) und der elektrische Widerstand von Polyamiden und von Vinylidenchlorid-Vinylchlorid-Copolymeren sowie der Einfluss der Ultraviolettbestrahlung auf diese beiden in den genannten Polymeren auftretenden Erscheinungen wurde untersucht. Die UV-Bestrahlung beeinflusst Lumineszenz und Widerstand der beiden Polymerarten auf verschiedene Weise. Bei Polyamiden führt die UV-Bestrahlung zu einer Abnahme von Phosphoreszenzdauer und Widerstand. Die erste der beiden Erscheinungen geht auf die Bildung von Radikalen und deren darauffolgende Oxydation zurück, die zweite auf eine Spaltung intramolekularer Wasserstoffbrückenbindungen im amorphen Teil des Polymeren, wodurch die Kettenbeweglichkeit und der Protonentransfer durch geeignete Orientierung der Segmente im elektrischen Feld erhöht wird. Die UV-Bestrahlung chlorhältiger Vinylpolymerer verursacht die Bildung von Vinylenketten und führt zu einer erhöhten Lumineszenzfähigkeit und einer Abnahme des Widerstandes. Die gebildeten Radikale werden leichter und ohne Veränderung der Vinylensequenzen oxydiert, so dass hier die Lumineszenz durch die Radikaloxydation nicht verschwindet.

Discussion

R. Buvet (*Ecole de Physique et Chimie, Paris, France*): Vous avez mentionné l'hypothèse donnée par certaines auteurs, d'une conduction protonique dans les polyamides. Je voudrais mentionner que les études que nous avons faites en collaboration avec Yu Liang-Tsé nous ont permis de conclure que probablement deux régimes distincts de conductivité pouvaient exister selon les conditions experimentales: taux d'humidité et température (*C. R. Acad. Sci.*, **254**, 110 (1962)). Seule la conductivité observable à température et/ou taux d'hydratation élévés est de toute évidence de nature ionique; les valeurs de conductivité sont alors supérieurs à 10^{-9} ohm^{-1} cm^{-1}.

En dessous de ces valeurs, l'absence de régimes transitoires ou leur nature strictement ionique impose de ne pas rejéter à priori une interprétation électronique pour le phénomène de transport de courant.

M. Kryszewski: Je suis d'accord avec les remarques de M. Buvet. Nous avons observé aussi les phénomènes indiqués par M. Buvet en étudiant la polarisation de nos échantillons en fonction du temps et la tension appliquée. Ces phénomènes ont une allure différente pour les polyamides et les polymères vinyliques ou le mécanisme de la conduction est lié aux éléctrons mobiles (doubles liaisons conjuguées).

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1429–1435

Étude de la Conductibilité Éléctrique de Films d'Acide Desoxyribonucléique

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Introduction

Le présent travail a pour objet l'étude de la conductivité en courant continu de films deshydratés d'acide desoxyribonucléique (ADN) entre 20 et 150°C.

Il a été entrepris à l'origine comme préliminaire d'une étude sur les propriétés diélectriques de films d'ADN. Il est en effet important de connaître la conductivité en courant continu d'un échantillon, ainsi que ses variations en fonction de la température, pour pouvoir interpréter des résultats d'absorption diélectrique. De plus on sait l'intérêt porté depuis quelques années sur les propriétés électroniques des biopolymères, entre autres la semi-conduction électronique grâce à laquelle on pourrait expliquer les phénomènes de transfert énergétique sur une distance non négligeable. Les premiers résultats sur la conductivité électrique de l'ADN ont été publiés en 1960 par Duchesne et collaborateurs,[1] depuis est parue l'étude de Eley et Spivey.[2] Les conclusions de ces derniers auteurs ne concordant pas complètement avec nos résultats nous ont incité à les présenter. Notre objectif initial nous a orienté vers une technique de mesure qui possède quelques particularités qu'il nous semble utile de développer au préalable.

Technique de Mesure

La Figure 1 représente schématiquement le dispositif utilisé. Deux bandes de platine écartées de 0,5 mm constituent les deux électrodes; elles sont maintenues sur une lame de silice fondue par un parallélépipède de Teflon qui, grâce à un système de ressort, applique également la lame isolante sur une plaque en laiton. Cette plaque est munie sur sa face inférieure d'un serpentin à circulation d'huile en communication avec un thermostat. On a creusé dans le bloc en Téflon une cuvette qui découvre la partie centrale des bandes de platine sur une longueur de 30 mm et dans lesquelles on introduit les solutions d'ADN qui sont ensuite évaporées.

Cet ensemble est placé dans une cloche à vide où la pression peut être réduite à une valeur inférieure à 10^{-5} mm Hg. La Figure 2 représente le circuit électrique de mesure. Il permet d'inverser la polarité de la pile et

de faire varier la tension de mesure suivant les rapports 1–10–100–1000. L'électromètre à condensateur vibrant utilisé (EKCO N 616B) permet la mesure de courants très faibles (limite théorique 10^{-16} amp). En prenant en considération le bruit de fond et la résistance de fuite introduite par les

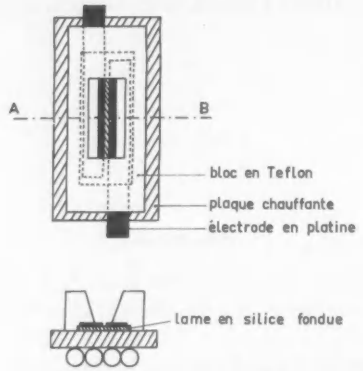

Fig. 1. Cellule de mesure (schématique). Les électrodes sont constitués de deux bandes de platine de 0,05 mm d'épaisseur, écartées l'une de l'autre de 0,5 mm. La plaque chauffante est une plaque en laiton sur laquelle est soudé un serpentin à circulation d'huile.

isolants nous estimons à 10^{16} ohms la limite supérieure de mesure de notre installation.

L'échantillon est introduit en petite quantité sous forme d'un gel concentré (1% d'ADN en poids) préalablement dégazé. La cloche est ensuite fermée après avoir introduit un desséchant (silica gel), la dessication dure

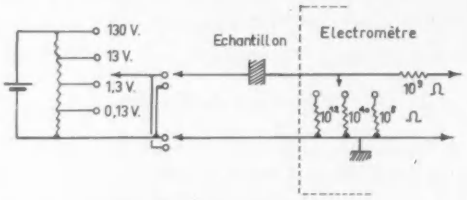

Fig. 2. Circuit électrique de mesure.

un jour. Ces opérations sont renouvelées deux à trois fois suivant la concentration et la quantité de gel introduite; en fonction de ces deux derniers paramètres on connait la quantité d'ADN existant dans la cellule. On fait ensuite le vide dans l'enceinte (pression inférieure à 10^{-5} mm Hg) pendant une journée, puis on applique la tension de mesure laquelle ne sera plus modifiée pendant toute la durée du cycle de mesure, à l'exception des échantillons pour lesquels nous avons vérifié la validité de la loi d'Ohm.

Les mesures électriques ne sont entreprises que le lendemain, toujours sous vide moléculaire. Ayant constaté des phénomènes de polarisation importants nous suivons les variations de l'électromètre grâce à un enregistreur. Lorsqu'on veut vérifier que la conductivité mesurée est indépendante du champ électrique on le fait varier suivant les valeurs 2,6, 26, 260,2600 v/cm. Pour les valeurs les plus basses les courants à mesurer sont très faibles. Ceci nous a contraint à faire cette vérification à haute température (90°C) et à soustraire le courant de polarisation ou de dépolarisation du courant total afin d'obtenir le courant de conduction réel. Le courant retenu pour un point est la moyenne de sept mesures effectuées à des temps égaux après inversion de la tension de mesure.

Le type de cellule employé entraîne des inconvénients, entre autres un facteur géométrique défavorable. En effet l'épaisseur des films d'ADN est de 0,1 mm environ, la constante de cellule est donc voisine de 2, il ne s'agit là évidemment que d'un ordre de grandeur en raison des difficultés de mesure de l'épaisseur de l'échantillon et de l'inhomogénéité du champ électrique. De plus il est probable que l'état de surface du film joue un rôle non négligeable dans la conductivité mesurée.

Cette structure se traduit cependant par un certain nombre d'avantages sur celles de type "sandwich." Elle permet un échange gazeux très facile entre l'échantillon et le milieu extérieur, ce fait est très important pour des produits hydrophiles comme l'ADN et où la moindre trace d'eau entraîne des variations considérables de conductivité. De plus l'évaporation lente aboutit à la formation d'un film parfaitement transparent et homogène qui adhère fortement à la fois au quartz et au platine, éléments très favorables pour la nature et l'efficacité des contacts électriques et thermiques.

Résultats

Les mesures ont porté sur 18 échantillons d'un même stock d'ADN de thymus de veau préparé par le Centre de recherches sur les macromolécules de Strasbourg. Sur ces 18 échantillons, trois ont été dialysés contre de l'eau distillée, un contre Mg Cl_2 10^{-3} M, le dernier, non dialysé, a été dégradé par traitement thermique (2.5 heures à 110°C dans un tube en pyrex scellé).

Nous avons représenté sur la Figure 3 une courbe typique de la variation du logarithme de la conductivité σ en fonction de l'inverse de T entre 20 et 95°C. On peut voir sur ce graphique que la conduction du cours de la première montée en température est beaucoup plus importante que celle mesurée au cours de la descente. A partir de 50°C environ la conductivité diminue lentement pour chaque température, nous avons pu suivre cette diminution à 95°C pendant 15 heures. Cette dérive n'est pas retrouvée pour la descente et les cycles thermiques suivants. Les points expérimentaux s'alignent alors suivant une droite de pente reproductible pour les différents cycles thermiques subis par un même échantillon. L'hysterèse de conduction avec le traitement thermique est retrouvée pour tous les

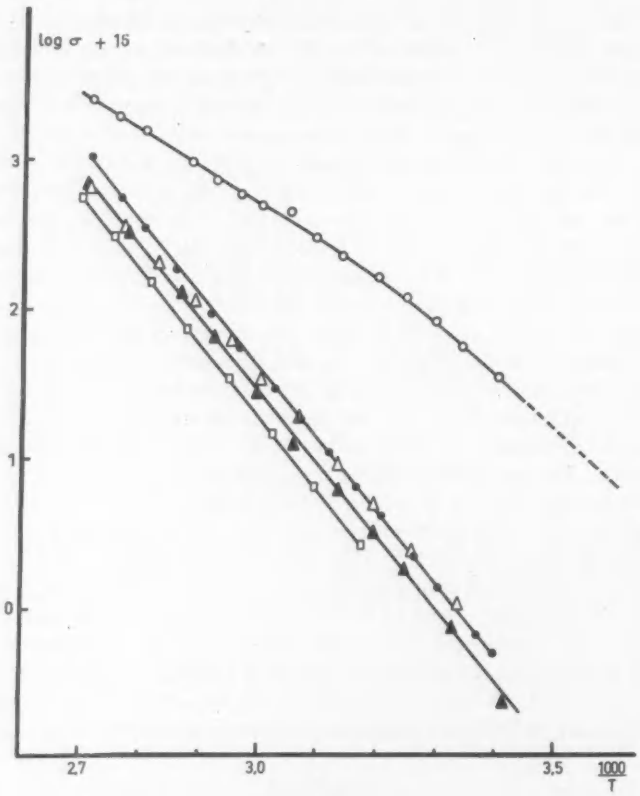

Fig. 3. Exemple de variations de la conductivité σ en fonction de la température T à tension de mesure 130 v: (○) premier chauffage; (●) premier refroidissement; (△) deuxième chauffage; (▲) deuxième refroidissement; (□) troisième refroidissement, tension de mesure 13 v.

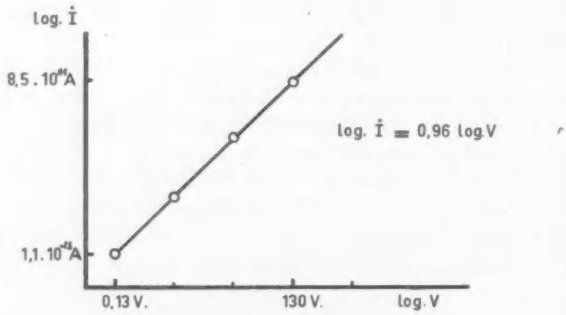

Fig. 4. Applicabilité de la loi d'ohm.

échantillons non dialysés, elle est beaucoup moins nette avec les échantillons dialysés.

Dans le domaine de tension utilisé (qui s'étend cependant sur 3 décades) l'effet du champ électrique sur la conductivité est négligeable. La Figure 4 montre par exemple la variation de $\log I = f(\log V)$. Les points expérimentaux s'alignent sur une droite de pente 0,96 au lieu du chiffre théorique de 1,0. Sur deux autres échantillons on trouve des droits de pente 0,93 et 1,05. Les écarts par rapport à la loi d'Ohm sont donc faibles, non systématiques, la Figure 3 montre également que la variation de la tension de mesure dans un rapport 0,1 ne modifie pas de façon significative la pente de la courbe $\log \sigma = f(1/T)$ (variation inférieure à 4%).

Le Tableau I résume les résultats concernant l'énergie d'activation de conduction E, et la conductivité à 90°C: σ_{90}. E est calculé directment d'après la doite $\log \sigma = f(1/T)$. Ne connaissant pas a priori le mécanisme de conduction il nous semble en effet préférable d'adopter une loi du type $\exp\{-E/RT\}$ plutôt que $\exp\{-E/2KT\}$. Il existe une dispersion des valeurs trouvées pour E et σ_{90}. Dans les cas où les différences sont significatives nous donnons les valeurs pour la première montée: E_M, et les descentes et montées suivantes qui sont alors superposables entre elles: E_D.

TABLEAU I

Echantillons	Energie d'activation		$\sigma_{90,M}$	$\sigma_{90,D}$
	E_M, eV	E_D, eV	10^{-16} mho	10^{-16} mho
Nondialysés	0,80 ± 0,20	0,95 ± 0,20	600–2500	40–350
Dialysé, H_2O	0,85 ± 0,20		2–8	0,5
Dialysé, $MgCl_2$	0,65		1	
Dégradé thermiquement	0,55		1	

Discussion

Nos valeurs de σ_{90} sont du même ordre que celles d'Eley et Spivey.[2] Il existe par contre une différence significative entre leurs données pour E (1,21 ± 0,025 eV, quand on ne tient pas compte du facteur 1/2 qui intervient dans le terme en exposant) et la nôtre (0,95 ± 0,20). Cette différence est peut-être le résultat de la disposition des électrodes, le type utilisé pour ce travail pouvant être à l'origine d'erreurs par états de surface. Il n'est pas exclu également que l'origine différente de l'ADN, donc la technique de préparation, puisse être une raison de ce désaccord. Signalons le meilleur accord avec le chiffre obtenu par Duchesne et collaborateurs[1] (0,80 eV), malgré des conditions expérimentales fort différentes (échantillons hétérogènes non complètement deshydratés).

Dans aucune de nos expériences la mesure de la conductivité électrique en courant continu n'a permis de mettre en évidence une transition de structure réversible de films d'ADN deshydratés entre 20 et 150°C, recherche qui était un de nos objectifs de départ. Par contre la conductivité au cours de la première montée en température est beaucoup plus

importante que celle obenue pour les cycles suivants, ceci sur tous les échantillons non dialysés, malgré une dessication antérieure prolongée et une géométrie favorable à cette dessication. Il semble qu'un départ d'eau lors du premier chauffage puisse expliquer cette hypothèse; la quantité d'eau en cause doit alors être faible, on ne peut en effet, par thermogravimétrie sous vide, mettre en évidence une perte de poids lors du chauffage; par contre, par chauffage on peut détecter une augmentation de pression dans une enceinte étanche, contenant un échantillon d'ADN préalablement soumis à un vide moléculaire prolongé, cette augmentation de pression apparaissant dans la zone (50–95°C) qui correspond à la dérive de la conductivité. On peut donc déduire que le premier chauffage entraîne le départ d'un gaz ou d'une vapeur en très petite quantité, ceci quelque soit le soin apporté à la dessication et au dégazage à la température ambiante. On peut supposer alors que ce départ est la cause de la diminution de la conductivité. Dans l'hypothèse où il s'agit d'eau, celle-ci serait fortement liée à la macromolécule.

Dans toutes nos mesures nous avons observé une polarisation importante, surtout sur les échantillons non dialysés, c'est-à-dire les plus conducteurs. Cette polarisation persistante se traduit par exemple par l'existence d'un courant de décharge lorsqu'on courtcircuite la pile, courant inverse au courant initial dont la décroissance est très lente (plusieurs heures, voire quelques jours). Ce courant décroit très rapidement dans les premières minutes, ce fait peut faire croire à l'absence de phénomènes de polarisation lorsque la sensibilité de l'instrument de mesure est insuffisante. L'existence de cette polarisation est la traduction de phénomènes de transport ionique au sein de l'échantillon et de charges d'espace au voisinage des électrodes, elle n'est pas une preuve de conduction ionique,[3] de même que l'absence de polarisation n'est pas une preuve suffisante de conduction électronique.

Cette polarisation peut cependant perturber la traduction macroscopique d'une conduction électronique, même à température élevée en raison de l'augmentation de la mobilité ionique. Nos résultats ne nous permettent pas de déterminer le type de conduction. En effet l'échantillon dialysé présente bien une conductivité négligeable, en comparaison de celle des échantillons non dialysés, mais on retrouve ce phénomène pour l'échantillon dégradé thermiquement qui a pourtant conservé son stock ionique initial.

Par ailleurs on sait que l'ADN en solution est dénaturé lorsque la force ionique devient trop faible ($<10^{-3}M$ ClNa à la température ambiante)[4] ce qui est le cas des solutions dialysées. On doit donc admettre que la structure native de l'ADN est indispensable à l'existence du processus de conduction. Sachant que Mg^{++} stabilise la structure de l'ADN malgré une faible force ionique,[5] le résultat sur l'échantillon dialysé contre MgCl $10^{-3}M$ serait en faveur d'une conduction par porteurs ioniques. Néanmoins il est souhaitable que des arguments expérimentaux complémentaires permettent de mieux préciser la nature et la mobilité des porteurs. En tout cas il ne semble pas possible de déduire un mécanisme de conduction dans l'ADN à partir des données expérimentales actuellement disponibles.

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Résumé

L'étude de la conductivité électrique de films deshydratés d'ADN en fonction de la température présente de nombreuses difficultés, notamment dues à celle d'établir de bons contacts électriques et de mesurer des courants de très faible intensité. Malgré cela, on peut dégager quelques résultats de l'expérimentation réalisée actuellement. (*1*) Après le premier cycle de chauffage, on observe une diminution importante de la conductivité. La deshydratation préalable avait été réalisée pendant 48 heures sous silica gel, puis 12 heures sous vide moléculaire. Parmi les explications proposées pour expliquer le précédent résultat figure la désorption d'un gaz. (*2*) Dans les limites de l'expérimentation (20 − 150°C), on peut représenter les variations de la conductivité σ par une loi de la forme: $\sigma = \sigma_0 C^{-E/nT}$, où $E = 0{,}95 \pm 0{,}2$ eV. Cette variation est monotone. Elle ne subit aucune transition brusque. (*3*) A 90°C, la résistivité de nos échantillons est de l'ordre de 10^{13} ohms-cm. Quand les films de DNA sont préparés à partir d'une solution dialysée, la résistivité, supérieure à 10^{16} ohms-cm., n'est plus mesurable. Ce résultat tend à montrer que la conductivité étudiée est de nature ionique.

Synopsis

The electric conductivity of dehydrated films of ADN has been studied in function of the temperature; the main difficulties reside in establishing good electrical constants and measuring currents of very low intensity. Nevertheless, some results of experimentation can be pointed out: (*1*) after a first cycle of heating up, the conductivity decreases appreciably. A previous dehydration has been carried out during 48 hr over silica-gel, and 12 hr in molecular high vacuum. This result can be explained by gas desorption. (*2*) Between 20 and 150°C. the conductivity variations σ can be expressed by $\sigma = \sigma_0 C^{-E/nT}$ where $E = 0.95 \pm 0.2$ eV. This variation is monotonic, and undergoes no sharp transition. (*3*) At 90°C. the resistivity of our samples is 10^{13} ohms-cm. When the films of DNA are prepared from a dialyzed solution, a resistivity, higher than 10^{16} ohms-cm., cannot be measured. This result would signify that the nature of the conductivity is of ionic character.

Zusammenfassung

Die Untersuchung der elektrischen Leitfähigkeit deshydratisierter ADN-Filme in Abhängigkeit von der Temperatur bietet zahlreiche Schwierigkeiten, besonders bei der Herstellung guter elektrischer Kontakte und der Messung sehr schwacher Ströme. Trotzdem können einige gesicherte Ergebnisse angeführt werden: (*1*) Nach dem ersten Erhitzungscyclus wird eine bedeutende Erniedrigung der Leitfähigkeit festgestellt. Die Vortrocknung wurde durch 48 Stunden über Kieselgel und dann durch 12 Stunden im Molekular-Vakuum durchgeführt. Als Erklärung des angeführten Ergebnisses wurde unter anderem die Desorption eines Gases vorgeschlagen. (*2*) In dem untersuchten Bereich (20–150°C) kann die Temperaturabhängigkeit der Leitfähigkeit σ durch eine Beziehung von der Form $\sigma = \sigma_0 C^{-E/nT}$, wo $E = 0{,}95 \pm 0{,}2$ eV, dargestellt werden Es handelt sich um eine monotone Abhängigkeit, ohne jede Umstetigkeit. (*3*) Bei 90°C beträgt der spezifische Widerstand der Proben etwa 10^{13} Ohm. cm. Bei DNA-Filmen, die aus einer dialysierten Lösung dargestellt wurden, liegt der spezifische Widerstand oberhalf 10^{16} Ohm. cm und ist nicht mehr messbar. Dieses Ergebnis scheint zu beweisen, dass es sich bei der untersuchten Leitfähigkeit um eine Ionenleitfähigkeit handelt.

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Sur le Rôle eventuel des Doublets Electroniques dans le Comportement Quantique des Biopolymères

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I. INTRODUCTION

Au cours des dernières années, de nombreux auteurs ont expérimenté le comportement quantique des biopolymères en supposant qu'il affecterait des expressions physiques spécifiques des interactions de leurs constituants organiques.[1–4] Les résultats obtenus dans tous les ordres d'expériences sont discutables parce que des facteurs extrinsèques mésestimés ou ignorés donnent l'apparence de propriétés qui ne sont pas alors directement liées à la composition et à la structure du biopolymère.[5,6]

Dans le domaine optique, où l'observation suppose une intervention énergétique préalable qui suscite des processus quantiques au niveau des motifs monomères, il n'est pas possible de distinguer des expressions manifestes des interactions, comme il s'en produit couramment sur les agrégats cristallins.[6,7]

Bien sûr, on relève, en émission différée notamment, des différences de comportement optique. Mais, en l'état actuel de la technique et de nos connaissances théoriques, il est bien difficile d'en tirer des conclusions sur la dynamique quantique macromoléculaire. C'est que la dynamique des molécules plus simples, des "motifs" monomères en particulier, est elle-même encore assez mal connue. En dehors des configurations les plus probables de la molécule, on manque de renseignements sur d'autres configurations possibles et à fortiori sur l'influence que pourraient avoir sur elles la polymérisation et l'organisation des polymères.

Cependant, l'exploration récente des régions spectrales correspondant à des transitions électroniques éventuellement génératrices de modifications structurales sensibles nous ouvre des perspectives encourageantes.[8] Elle attire notre attention sur le rôle quantique des électrons des doublets libres (lone pairs) qui ne tiennent qu'une rôle accessoire ou épisodique dans leur molécule d'origine, mais contractent des liaisons secondaires quand les molécules font partie de chaînes polymères.

C'est ce rôle éventuel, puis certaines de ses incidences structurales que nous avons tenté d'étudier sur certains amino-acides et polypeptides, au moyen de la spectrométrie d'émission optique et de la spectrométrie hertzienne.

II. TECHNIQUES EXPERIMENTALES

A. L'Optique d'Emission aux Très Basses Températures

Les amino-acides et les protéines sont optiquement excitables dans différentes régions de l'ultra-violet et, en particulier, entre 2800 et 3650 A. Les spectres d'absorptions correspondants culminent entre 2800 et 2900 A. et présentent une densité optique négligeable au delà 3500 Å.

Cependant, aux très basses températures ($<-100°C$), les amino-acides et les protéines excités à ces différentes longueurs d'onde émettent une luminescence de longue durée visible, enregistrable, et dont la durée permet d'étudier le déclin.

Ces différentes observations ont été effectuées à l'aide d'un spectrophosphorimètre Aminco; cet appareillage permet de tracer les spectres d'excitation et d'émission depuis la température de l'azote liquide jusqu'à la température ambiante.

Un phosphoroscope permet de discriminer la phosphorescence ($\tau \geqslant 10^{-3}$ sec). La source excitatrice, constituée par un arc au Xénon XBO-162 stabilisée et alimentée en courant continu, délivre un spectre continu de brillance régulièrement croissante entre 2000 et 4000 A., et de brillance constante entre 4000 et 8000 A.

La sélection des fréquences d'excitation et d'émission entre 2000 et 8000 Å est réalisée par des monochromateurs à réseau (600 traits) de 50 × 50, permettant une résolution normale $\Delta\lambda/2 = 50$ A. dans le montage de phosphorescence utilisé dans ce travail.

La détection s'opère au moyen de photo-multiplicateurs RCA IP 21 et IP 28 sélectionnés, alimentés sous 700 volts stabilisés électroniquement ou sous 900 volts sur piles.

L'enregistrement des spectres d'excitation et d'émission est obtenu automatiquement et après amplification sur un X-Y (Electro-Instrum). Les déclins de luminescence sont photographiés sur oscilloscope Tektronix (type 502) à l'aide d'une caméra Polaroid.

L'ouverture ($f/4$) des monochromateurs et la simplicité des trajets optiques rendent compte de la luminosité élevée de cet appareil. Les valeurs rapportées n'ont pas été corrigées. L'absence de correction rend compte des écarts qui peuvent exister entre les maxima d'excitation de fluorescence et ceux classiquement obtenus en absorption.

Cette chaîne de mesures nous a permis, dans un premier temps d'établir les caractéristique optiques d'émission des principaux amino-acides et de protéines albuminiques.[7]

L'expérimentation des amino-acides aliphatiques, dépourvus de liaisons conjuguées, nous a notamment permis de désigner des transitions $n \rightarrow \pi^*$ comme responsables en l'occurrence de l'émission différée. L'émission différée s'effectue principalement par "fluorescence lente" aussi bien dans le cas des protéines que dans celui des amino-acides optiquement excités.

Tout se passe ainsi comme si la désactivation radiative de certains électrons excités s'opérait directement d'un état triplet jusque vers une con-

figuration différente de celle qui s'identifie à l'état fondamental initial. C'est ce que tente de schématiser le diagramme énergétique (Fig. 1).

Avec les moyens techniques dont on disposait au laboratoire, nous avons tenté de vérifier l'existence de cette configuration métastable. Pour cela, nous avons tenté d'exploiter les résultats obtenus en émission aux très basses températures (étude comparative de déclins de luminescence pour différentes radiations excitatrices). On a procédé à des essais de thermoluminescence pour détecter éventuellement l'émission résultant de la désactivation de la configuration M, lors du réchauffement. Ces essais ont été pratiqués avec des photo-multiplicateurs sensibles aux radiations visibles.

Et, enfin, tablant sur l'éventuelle nature radicalaire de la configuration supposée nous avons combiné l'excitation optique et la résonance paramagnétique électronique.

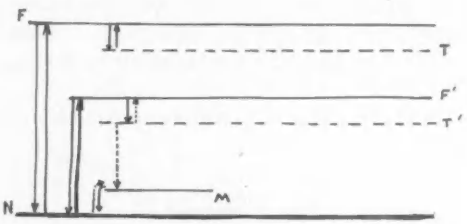

Fig. 1. Transitions $N \rightarrow F$, $\pi \rightarrow \pi^*$; $N \rightarrow F'$, $n \rightarrow \pi^*$.

Notre spectromètre Varian (100 KC) est équipé d'une cavité à température variable (soumise à des températures comprises entre 77 et 373 °K) et comportant une fenêtre d'irradiation. Dans ces conditions, il est possible de porter les sondes de quartz contenant l'échantillon à la température de l'azote liquide, et de les irradier in situ.

L'irradiation s'effectue au moyen d'un arc à vapeur de mercure (Osram H B0.200 haute pression) dont le maximum d'émission se situe vers 3650 A., et dont les radiations ont été dans quelques expériences sélectionnées au moyen de filtres interférentiels.

La durée des expositions à la lumière n'excède jamais cinq minutes. Les échantillons au préalable dégazés et maintenus sous vide émettent alors un signal de résonance dont l'intensité croît progressivement mais lentement.

Après que cesse une exposition, l'échantillon se désactive radiativement. C'est à l'issue de cette désactivation que nous effectuons le relevé d'éventuels signaux de résonance.

Au début de nos expériences, nous avons utilisé du tryptophane racémique chromatographiquement pur, à l'état de microcristaux.

Nous avons ensuite réalisé des solutions de ce composé dans le mélange classique éther–pentane–alcool (E.P.A.). Ces solutions congèlent sans cristalliser; ceci permet d'une part de procéder aux irradiations dans de

bonnes conditions, et, d'autre part, d'éviter que la cristallisation modifie les processus qui résultent de l'excitation optique.

B. La Détection d'une Eventuelle Configuration Radicalaire au moyen de la Résonance Paramagnétique Électronique

Les transitions électroniques $n \rightarrow \pi^*$ ont la réputation de transformer sensiblement la configuration des molécules qui en sont le siège.[9] Ces transitions joueraient, semble-t-il, un rôle important dans l'évolution chimique des composés adoptant sous leur impulsion des configurations diracaloïdes radicalaires ou dipolaires.[8]

Nous avons utilisé la technique de résonance paramagnétique électronique pour tenter de vérifier si la configuration métastable, résultant éventuellement de la désactivation radiative d'amino-acides, était ou non radicalaire.

Nous étions encouragés dans cette détermination par les expériences de Ingram-Allen qui avaient détecté des signaux de résonance sur des protéines natives optiquement excitées par la radiation 3650 A., aux très basses températures.[10]

Nous avons choisi d'étudier le tryptophane dans les conditions expérimentales suivantes.

III. RESULTATS

A. Résultats Optiques

Comme on l'a déjà rappelé, les amino-acides aromatiques sont électroniquement excitables dans une gamme de fréquences qui s'étend de l'ultraviolet moyen à la limite du spectre visible. A la température de l'azote liquide, excité à deux fréquences fixes (2560 et 3650 A.) émises par un arc au mercure, le tryptophane se désactive radiativement.

L'excitation au moyen de la radiation 3650 A. provoque une émission différée qui est encore mesurable à la température normale (celle qui résulte de l'excitation à 2560 A. cesse de l'être vers $-80°C$), et dont le déclin est, de loin, le plus rapide. Sa cinétique depend peu de la température entre 77 et 150°K. (Fig. 2).

Tout se passe comme si la désactivation s'opérait directement et avec une grande probabilité vers une configuration qui devrait être différente de la configuration normale.

Cette configuration n'a, à notre connaissance, jamais été décrite: sa formation temporaire ne serait pas en contradiction avec les conséquences structurales de l'excitation optique engendrant des transitions $n \rightarrow \pi^*$.

A l'issue de la désactivation radiative qui se produit à la température de l'azote liquide, une montée progressive de la température ne s'accompagne d'aucune émission optique mesurable entre 2000 et 7000 A. Actuellement, nous mettons au point un système de détection des quanta infra-rouges qui pourraient éventuellement être émis au cours du réchauffement. De même,

l'analyse thermique différentielle, depuis la température de l'azote liquide jusque vers des températures de l'ordre de 100 °C, est en cours de mise au point au laboratoire.

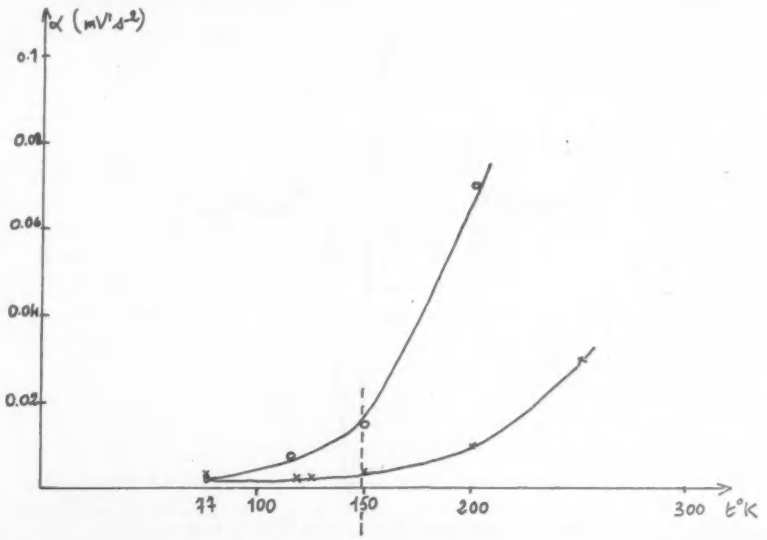

Fig. 2. Excitation du tryptophane, au moyen de la radiation (O) 2560 A. et (×) 36-50 A.

Ainsi, si configuration dynamique il y a, l'énergie excédentaire qu'elle détient par rapport à celle de la configuration initiale, serait de l'ordre de quelques Kilocalories/mole.

B. Résultats Magnétiques

Dans la cavité du spectromètre maintenue à la température de l'azote liquide, le tryptophane à l'état cristallin, préalablement exposé à la radiation 3650 A., puis ayant subi la désactivation radiative, présente un signal de résonance paramagnétique électronique. Ce signal est composite: il est constitué d'un signal thermostable, résultant sans doute d'un dommage irréversible., et d'un signal thermolabile. Ce dernier disparaît vers −160°C. Les échantillons de tryptophane sont chromatographiquement purs, et il est peu probable que les signaux de RPE soient dus à des impuretés. Par contre, l'état microcristallin, le désordre qui le caractérise, n'excluent pas que les signaux labiles soient dus à des centres *F*. C'est pour cette raison que l'on a expérimenté les molécules de tryptophane dispersées dans un système solvant qui congèle sans cristalliser.

La Figure 3 retrace le signal de résonance paramagnétique thermolabile alors obtenu dans des conditions précisées dans la légende.

Ce signal est mesuré après que les molécules excitées se sont désactivées radiativement. Au cours de la remontée de température qui fait disparaître le signal, il est impossible de détecter l'émission de photons (dont la longueur d'onde est comprise entre 3000 et 7000 A.).

Fig. 3. Signal de resonance paramageré tigue de tryptophane.

Enfin, on doit signaler qu'au cours de la désactivation radiative, l'intensité du signal qui était apparu lors de l'irradiation et était sensiblement stabilisé, augmente, puis demeure constante à la fin de la désactivation tant que la température demeure invariable.

IV. DISCUSSION

A. Sur l'Existence d'une Configuration Métastable Résultant de Transitions $n - \pi^*$

1. Soupconnée par l'optique d'émission aux basses températures. L'émission différée qui résulte de l'excitation optique des amino-acides par la radiation 3650 A. d'un arc au mercure présente certains caractères attribués habituellement aux transitions $n \rightarrow \pi^*$ (fréquence d'excitation proche du visible, taux de conversion interne du quantum très élevé, différence entre fréquences émises par fluorescence et phosphorescence).

La désactivation radiative de longue durée est associée à l'existence d'un état triplet. Cet état se désactive, semble-t-il, en partie tout au moins, par fluorescence lente. C'est ce que paraît indiquer la Figure 1, où l'on voit que la cinétique est peu influencée par la température, au moins jusque vers 150°K. Ensuite, cette cinétique évolue progressivement et non pas d'une manière brutale.

C'est à cause de ces caractéristiques que nous sommes amenés à soupçonner l'existence d'une configuration dynamique résultant de la désactivation radiative de la molécule optiquement excitée.

Comme on l'a dit précédemment, nous n'avons pas encore d'autres preuves optiques de l'existence d'une telle configuration. Nous les cherchons actuellement mais, déjà, les résultats obtenus par résonance paramagnétique électronique paraîssent apporter une première confirmation à notre hypothèse de travail.

2. Mise en évidence, sur le tryptophane, par la résonance paramagnétique électronique. Lorsque les molécules de tryptophane, isolées les unes des autres dans un milieu solvant qui congèle sans cristalliser, sont optiquement excitées, puis se sont désactivées en réémettant un photon, on observe à 77°K un signal de résonance paramagnétique électronique stable.

En fait, ce signal est thermolabile. Il disparaît vers 150°K et l'on notera que cette température correspond sensiblement à celle où se produisait un changement prononcé dans la cinétique de désactivation radiative.

Actuellement, l'un de nous étude systématiquement le signal et, à travers lui, la configuration moléculaire qu'il est sensé représenter.

Cette configuration survit normalement à l'état triplet qui l'a engendrée par sa désactivation. Le quantum d'énergie supplémentaire qu'elle détient par rapport à l'énergie de la configuration normale est faible (du domaine infra-rouge, vibrationnel, phonons).

Est-ce à dire que la configuration radicalaire pourrait être engendrée par irradiation infra-rouge, comme cela se produit déjà chez certains composés à la fois photochromes et thermochromes?[11] L'expérience nous renseignera sur ce point.

On conçoit aisément la portée de sa réponse: affirmative, elle rangerait les configurations métastables dans le domaine accessible à l'énergétique biochimique.

B. Les Configurations Métastables Détentrices de Phonons et les Biopolymères

Il paraît avoir, on l'a bien vu, une corrélation entre les transitions qui affectent les électrons des doublets libres et l'existence de configurations dynamiques métastables détentrices de quanta vibrationnels (phonons).

Ces doublets (ceux notamment des groupes C=O et N—H des peptides) sont directement concernés par les liaisons secondaires qui résultent de la polymérisation des amino-acides. Leur probabilité de transition doit en être affectée, et par voie de conséquence, la formation et les caractères des configurations qui en résultent.

Déjà, si l'on compare les quelques données optiques d'émission des biopolymères et de leurs constituants isolés, on relève des différences significatives de leurs caractéristiques (intensité, durée, cinétique). Ce qui nous incite à poursuivre ce travail comparatif en nous intéressant spécialement aux configurations qui pourraient résulter de la désactivation radiative.

Ce travail a été effectué grâce a la convention de recherches attribuée au laboratoire par la Délégation Générale à la Recherche Scientifique et grâce au concours du Centre de Recherches du Service de Santé des Armées.

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Résumé

Les biopolymères, et notamment les protéines globulaires, assurent le transfert de l'énergie chimique. Cette dernière emprunte le réseau polypeptidique en suivant des itinéraires et des mécanismes quantiques encore inconnus. L'attention des auteurs intéressés par ce double problème a été attirée par les électrons des "doublets libres" qui ne tiennent qu'un rôle accessoire ou épisodique dans leur molécule d'origine mais participent aux liaisons qu'elle établit avec les partenaires d'une autre chaîne polymère. Des expériences optiques (spectrométrie d'émission) permettent d'établir les caractéristiques des transitions dont les "doublets" sont l'objet et de discuter de leurs conséquences sur nos conceptions du comportement quantique des molécules libres et polymérisées. Ces expériences ont comme suite logique la recherche, au moyen de la résonance paramagnétique électronique, de configurations radicalaires métastables, éventuellement issues de l'excitation optique. L'ensemble de ces travaux réalisés actuellement sera exposé et on tentera de dégager les perspectives sur le problème du comportement quantique des biopolymères.

Synopsis

Biopolymers, especially globular proteins, are responsible for chemical energy transfer. This energy proceeds through the polypeptide network by following quantum mechanisms and pathways unknown up to now. The attention of the authors was kept on the presence of the electrons of the 'free doublets' which play only a secondary role in their molecule of origin but participate in establishing bonds with the partners of another polymer chain. Optical experiments (emission spectrometry) make it possible to determine the transition characteristics which affect these 'doublets' and to discuss their consequences upon our ideas about the quantum behavior of free and polymerized molecules. As logical consequence these experiments suppose the research by means of EPR method, of metastable radical configurations, eventually formed by optical excitation. The researches will be exposed, and an attempt will be made to give some perspectives about the quantum behavior of biopolymers.

Zusammenfassung

Die Biopolymeren und besonders die Globularproteine sichern die Übertragung von chemischer Energie. Diese wird dem Polypeptidnetz über noch unbekannte Wege und Quantenmechanismen entnommen. Durch das Interesse an diesem doppelten Problem wurde die Aufmerksamkeit der Autoren auf die Elektronen in "freien Dubletts" gerichtet, die in ihrer ursprünglichen Molekel nur eine nebensächliche Rolle spielen, aber an Bindungen zu Partnern einer anderen Polymerkette teilnehmen. Optische Versuche (Emissionspektroskopie) erlauben die Festlegung der Übergangscharakteristik der "Dubletts" sowie die Diskussion der Folgerungen für die Vorstellungen über das quantenhafte Verhalten der freien und polymerisierten Molekel. Diese Versuche führen zu einer elektronenresonanzspektroskopischen Untersuchung der metastabilen Radikalkonfigurationen, die bei der optischen Anregung gebildet werden. Die Gesamtheit der durchgeführten Arbeiten wird besprochen und ein Ausblick auf das Problem des quantenhaften Verhaltens der Biopolymeren gegeben.

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On Electrical Asymmetry at the Junction of Cationic and Anionic Permselective Membranes

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A. INTRODUCTION

Cation-exchange (cationite) and anion-exchange (anionite) polymers in the form of membranes can be joined in various configurations. Let us define an *amphoteric* membrane as one whose cationite and anionite regions are so intermingled that they are physically indistinguishable and may even be appended to the same macromolecule. A *mosaic* membrane is a single ion-exchange membrane whose anionite and cationite areas are clearly defined and distinguishable. A *bipolar array* is a laminar conjunction of individual anionite and cationite membranes either physically touching or separated by a porous spacer. A *bipolar membrane* is an integral, laminar combination of anionite and cationite regions. If the junction between these two laminar regions is particularly sharp, the term step-junction bipolar membrane is used. All of these types exist and have diverse electrical properties. This communication describes the preparation of integral, bipolar membranes and compares the electrical asymmetry at junctions of step-junction membranes, bipolar membranes, and bipolar arrays.

There is a formal analogy between the conductance of an electrolyte in water and of electrons and holes in a semiconductor.[1] Hence, considering an ion-exchange membrane as a matrix of fixed ions of one sign neutralized by mobile ions of the opposite sign[2] leads to an analogy between the p–n junction in a doped semiconductor[3] and a bipolar membrane. This same analogy has been proposed for blocks of acid-doped and alkali-doped ice melted together.[4]

Various authors have qualitatively noted electrical asymmetry for bipolar arrays,[5–7] and one amplifying circuit has been reported.[8] It is not clear which type of configuration Frilette studied, and he did not consider the electrical implications of his observation. The asymmetry in the complex rubber diaphrams of Maslov and Ovodova which contained ion-exchange resins, alcohol, and manganese dioxide has been ascribed to the conjunction of the manganese dioxide with a tantalum oxide coating on their tantalum electrodes.[9]

Our first goal was to make the simplest possible system free of porous spacers. Our attention was brought to this problem by Mauro,[10] who has

published a formal analysis of the capacitance in a step-junction, bipolar membrane at equilibrium and who has done experimental work on bipolar membranes prepared in this laboratory. Secondly, we wished to test the explanation often advanced to explain the asymmetry at bipolar junctions. This salination–desalination hypothesis is based on a lower resistance at the junction when the mobile ions are forced inward (forward direction), and a higher resistance at the junction when the mobile ions are pulled out (reverse). The appropriate voltage, membrane, and ionic directions are shown in Figure 1. The analogous explanation for rectification at an

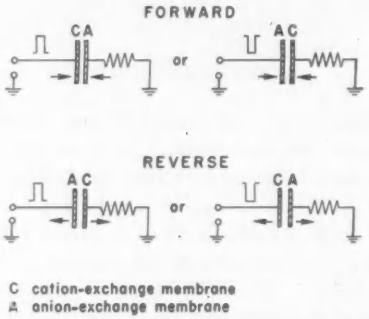

Fig. 1. Pulse, membrane, and ionic directions.

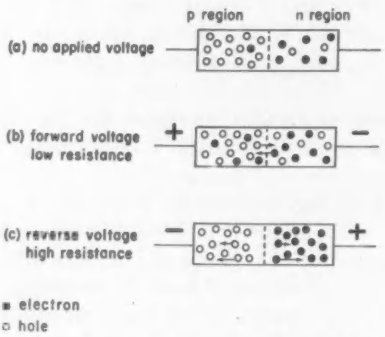

Fig. 2. Asymmetry in a p–n junction diode.

electronic p–n junction is shown in Figure 2. In the electronic situation the essential phenomenon is the injection of a sufficient number of minority carriers across the junction. Although the analogy of the electronic situation is helpful, it cannot be applied at too high a current flow.

B. PREPARATION OF BIPOLAR MEMBRANES

By the successive steps of swelling a polyethylene film with monomeric styrene, causing the styrene to polymerize in the film, and reacting the

graft copolymer so formed with a sulfonating agent or a chloromethylating agent followed by a tertiary amine, thermoplastic ion-exchange membranes of either type can be made.[11]

A cationite membrane 0.2 mm. in thickness (AMFion C-103) and an anionite membrane 0.15 mm. in thickness (AMFion A-104), each piece about 10 cm. square, are dried in an oven at 100°C. for 30 min.* The dry samples are placed on top of each other between sheets of aluminum foil and placed in between the plates of a laboratory molding press previously heated to 150°C. By carefully pressing this construction together at a pressure of about 35 kg./cm.^{2} for about 2–3 min. a permanent, integral, bipolar membrane is made. By shortening the molding time to 6–20 sec. a semipermanent membrane, capable of being peeled apart later with care, is made. The latter is termed a step-junction bipolar membrane. This molding procedure is facilitated, if aluminum foil coated with Teflon or the equivalent is available.

C. AREA-RESISTANCE

The area-resistance of single membranes, bipolar membranes, or bipolar arrays can be measured by placing them between mercury pools in the acrylic cell shown in Figure 3. This cell is then used in a standard Wheat-

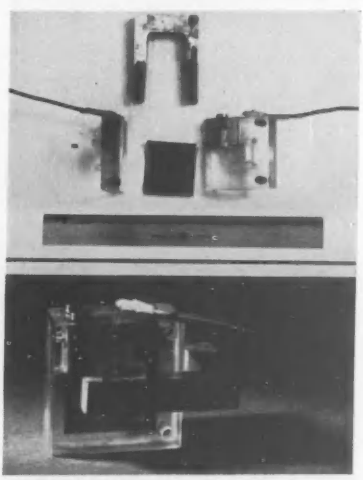

Fig. 3. Plastic cell for measuring area resistance.

stone bridge. It has been found that 1000 cycles/sec. is a suitable frequency. The area-resistance of a single ion-exchange membrane of the type under discussion does not vary when measured in equilibrium with 1:1

* Typical characterization of these membranes: area-resistance, 7 ± 2 ohm-cm.^{2}; dry capacity, 1.2 ± 0.1 meq./g.; water, 12 ± 2%; Mullen burst, 3–4 kg. cm.^{2}; permselectivity ($1N/0.5N$) 92 ± 4%.

electrolytes ranging in concentration from 1*M* to 0.001*M*[12,13] This value is typically 4–5 ohm-cm.^{2}. For electrolyte below 0.001*M* in strength, however, the area-resistance increases rapidly. The carefully washed samples employed in this report showed for the cationite 15–25 ohm-cm.^{2} and for the anionite 1500–3000 ohm-cm.^{2}. Values as high as 10,000 ohm-cm.^{2} are known for individual membranes washed for weeks.[14]

Our criterion of asymmetry was unequal resistance in the two directions of current shown in Figure 1.

D. EXPERIMENTAL

Comparison of Step-Junction and Highly Fused Bipolar Types

By using the cell pictured in Figure 3 with a 10-ohm resistor in series for measuring the current approximately 5 v. peak-to-peak, 60 cycles/sec. sinusoidal potential was impressed across a highly fused (2 min.) bipolar membrane. The current-voltage curve displayed on the x and y axes of

Fig. 4. Lack of asymmetry for a highly fused bipolar membrane.

Fig. 5. Asymmetry in a step-junction bipolar membrane.

an oscilloscope showed no asymmetry, as shown in Figure 4. The area resistance was 800 ohm.-cm.^{2}.

When a lightly fused (10 sec.) step-junction, bipolar membrane was used, a definite asymmetry of the type shown in Figure 5 was observed. Asymmetry was maintained when the frequency was changed to 1000 cycles/sec. At 60 cycles/sec. the average area resistance was 500 ohm-cm.^{2}; at 1000 cycles/sec., it was 175 ohm-cm.^{2}.

MEMBRANE ARRAYS

At the time these experiments were done the note of Lovrecek et al.[6] had been published. We endeavored to repeat their experiment using the same fabric-reinforced, highly crosslinked Nepton membranes (Ionics, Inc., Cambridge, Mass.) they had used in acid, and hydroxyl form with a Teflon-coated, porous glass cloth (AMFab TX10–40) 0.03 mm. thick in-between the membranes. With 3 v. of 60 cycles/sec. impressed across the cell and a 10-ohm resistor in series, asymmetry of the same type shown in Figure 5 was observed and continued to be observed, with a more open figure showing higher capacitance, at 600 and 6000 cycles/sec.

When the two Nepton membranes and spacer were washed in freshly distilled water for several hours, however, the voltage-current form of Figure 6 showing capacitance, but little or no asymmetry, was observed. A repetition with the Nepton membranes alone without porous spacer gave the same result.

Fig. 6. Symmetrical capacitance in a bipolar array.

When a pair of AMFion membranes, also highly washed was placed in the cell with the porous spacer in-between, subjection of this array to 3 v. of 60 cycle/sec. alternating current resulted in a straight-line Ohm's law with no capacitance. Repetition in the absence of the spacer gave the voltage-current form of Figure 7, a marginal result.

In order to follow up the observation that in the case of arrays of individual membranes the amount of saline impurity may be crucial, a pair

Fig. 7. Lack of asymmetry in an electrolyte-free array.

of highly washed AMFion individual membranes in acid and hydroxyl form were separately dried and separately equilibrated in a solution of potassium chloride $5 \times 10^{-5}M$ (4 mg./l.). Using 3 v. of 60 cycle/sec. alternating current and a 10-ohm resistor in series to measure the current, the voltage and current forms were individually displayed on a dual beam oscilloscope. Figure 8 shows the voltage on top of the current for the

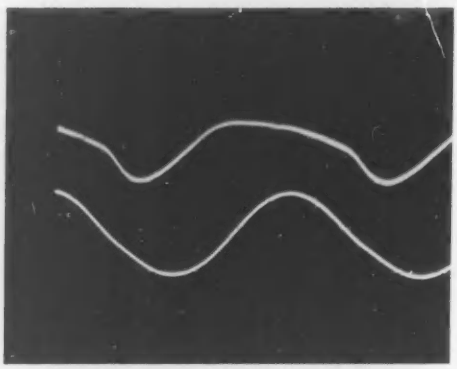

Fig. 8. Voltage and current forms, low salinity array, forward.

anionite member of the array toward the generator. Figure 9 shows the voltage signal above the current signal, when the cationite member is toward the generator. Since the array is capacitive, the current is seen to lag behind the voltage. In each case the asymmetry follows the scheme of Figure 1, that is the conductance is lower in the direction of desalination.

In addition to sinusoidal alternating current many experiments were performed with 1-v. pulses at 1000 pulses/sec. for various pulse lengths in the range of 5–50 μsec. Only slight asymmetry was observed.

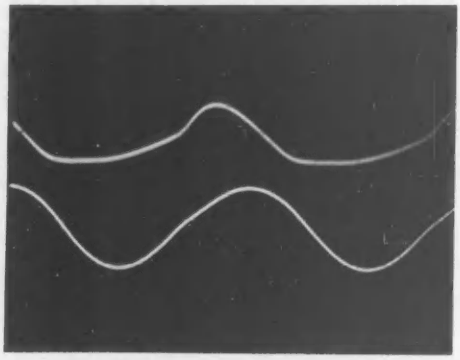

Fig. 9. Voltage and current forms, low salinity array, reversed.

The same pair of highly washed membranes without the highly dilute saline solution showed no asymmetry for either short pulses or alternating current.

An experiment was run in 0.001*M* potassium chloride at increasing frequency to see if at higher frequencies the distortion ascribed to the flux of coions could be eliminated. For signal strengths in the range of 2–4 v. across a pair of AMFion membranes some distortion of the type shown in Figures 8 and 9 was observed at 10–3000 cycles/sec. Above 4000 cycles/sec. no distortion of the impressed sine wave could be seen. With highly washed membranes no asymmetry was observed in the range of 60–600,000 cycles/sec.

E. DISCUSSION

The purpose of this work was to prepare an integral, bipolar membrane and to compare any asymmetry found therein with arrays of individual membranes. A quantitative theoretical analysis of both situations is a formidable task which has not been attempted.

As predicted by analogy to the electronic case a sharply defined step-junction, bipolar membrane represents a more favorable situation than does a complete fusion. When these two types are measured in strong electrolyte (0.6*M* potassium chloride), the step-junction will have an area resistance up to 20-fold higher than the normal bipolar fusion, showing a true environmental distinction. But asymmetry in the bipolar membrane apparently does not depend on trace concentration of coions[14] as reported here for arrays of membranes. This suggests that the mechanism beneath the asymmetry for bipolar membranes and bipolar arrays is different. In the bipolar membrane a "space charge layer" of polymer unneutralized by counterion may be crucial.[10] In the bipolar array a slight change in concentration of coion in the range of $10^{-5}M$ may be sufficient for asymmetry even though it is known that at higher concentrations of coion the resistance of a single ion-exchange membrane does not change.

Specifying the coion concentration for a membrane in a given solution is not straightforward, since it is known that the value is higher[15,16] than a Donnan calculation would suggest. Another effect perhaps ascribable to trace amounts of coion is the nonreproducibility of the capacitance in the system. Even at the low frequency of 60 cycles/sec. the capacitance as shown by the voltage-current curves for membrane arrays varied from zero to substantial (1 μf/cm.^{2}). The presence or absence of a porous spacer showed little change in either capacitance or asymmetry.

In addition to the possible formation of a space charge layer at the junction of a bipolar membrane or asymmetry due to the change in concentration of coion, a third consideration is asymmetry due to the energy of activation of the ionization of water.[6] With some coion present in the ion-exchange matrix, all the potential would be impressed across the thin layer of water between the individual members of a bipolar array. In that case one might expect to find asymmetry due to the relative ease of water formation from ions compared to ionization. In this report we have shown that in an array of highly washed membranes asymmetry is not demonstrated. This suggests that due to the high resistance of the cationite and anionite regions free of coion, there is not a large voltage gradient at the center.

To conclude, one may consider at least three possible explanations for the presence or absence of a rectifying effect at the junction of cationite and anionite membranes: formation of a space charge layer, differential resistance arising from the presence or absence of trace amounts of coion, energy of activation of ionization of water. In the step-junction, bipolar membrane the first may be operative. In a bipolar array, with or without porous spacer, the second may be operative due to the high resistivity of membranes free from coions. For this same reason the voltage gradient at the junction may be too low to allow asymmetry from the third explanation to be observed. The high resistivity of electrolyte-free membranes may arise from minute heterogeneities in their structure.

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Synopsis

Previously electrical asymmetries and amplification of signals have been reported for arrays of separate ion-exchange membranes, ion-exchange membranes in conjunction with insulation layers, and ion-exchange membranes mixed with metallic depolarizers. This communication describes the preparation of integral bipolar ion-exchange membranes, which are electrolytic analogues of *p–n* junctions, from thermoplastic sheets by compression molding. By use of this new, simplified junction, the question of asymmetrical, electrolytic resistance is examined for direct current and alternating current, and comparisons are made among junctions, arrays of dissimilar membranes. The salinization–desalinization mechanism generally advanced for explaining asymmetry is analyzed with relation to these data.

Résumé

On a parlé précédemment des assymétries électriques et de l'amplification de signaux par: des séries de membranes échangeuses d'ions séparées, des membranes échangeuses d'ions conjointement avec des couches isolantes et des membranes échangeuses d'ions mélangées avec des dépolarisants métalliques. Cette communication décrit la préparation de membranes "bipolaires" intégralement échangeuses d'ions et électrolytiquement analogues aux jonctions *p-n*, à partir de feuilles thermoplastiques de moulage par compression. En employant cette nouvelle jonction simplifiée, la question d'asymétrie et de résistance électrolytique est examinée pour du courant continu et du courant alternatif et on a fait des combinaisons entre ces jonctions, des séries de membranes dissemblable. Le mécanisme de salinisation–désalinisation généralement proposé pour expliquer l'asymétrie est étudié en fonction de ces résultats.

Zusammenfassung

Schon früher wurde elektrische Asymmetrie und Signalverstärkung beschrieben für getrennte Ionenaustauschermembrane, Ionenaustauschermembrane in Verbindung mit Isolierschichten, und Ionenaustauschermembrane gemischt mit metallischen Depolarisatoren. In der vorliegenden Mitteilung wird die Darstellung integraler "bipolarer" Ionenaustauschermembranen aus thermoplastischen Folien durch Druckverformung beschrieben, die elektrolytische Analoga zu *p-n*-Junctions darstellen. Mit diesen neuen vereinfachten Systemen wird die Frage des asymmetrischen Elektrolytwiderstandes für Gleichstrom and Wechselstrom untersucht und Vergleiche zwischen Junctions, unähnlichen Membranteilen. Anhand dieser Daten wird der allgemein zur Erklärung der Asymmetrie angenommene Salzungs-Entsalzungsmechanismus einer Analyse unterzogen.

Discussion

R. Buvet (*Ecole de Physique et Chimie, Paris, France*): Je voudrais demander à l'orateur s'il est possible de se procurer des échantillons de membranes bipolaires.

W. K. W. Chen: The materials used are available to all who are interested. We have been working together with other researchers, such as Dr. A. Mauro, to prepare better bipolar materials. We still have a great deal to learn to prepare good step-junction bipolar membranes.

E. Selegny (*Faculté de Nantes, France*): From your description it seems to me that your styrene was not really and anyway not fully grafted, but formed snack-cage poly-

mers in your polyethylene. It does not change your reasoning much, and I have already used such preparations myself.

W. K. W. Chen: I agree with Dr. Selegny that many of the so-called "graft" polymers described in the literature during the past few years are not true covalent graft polymers. We shall be presenting some new observations in our paper, *Comparison of Radiation- and Peroxide-Initiated Grafting of Styrene to Polyethylene Film*, tomorrow. Some of the graft copolymers prepared in the past, upon more careful fractionation, have been shown to be predominantly homopolymers.

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Polyvinylanthraquinone Redox Resins (Electron Exchange Polymers)

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Redox resins, polymers which possess the ability to be oxidized and reduced reversibly, have been known for about ten years. The group in the resin with the redox property can be of different nature. We would like to confine ourselves to resins possessing a quinone–hydroquinone redox system and which are insoluble and have limited swelling capabilities in water.

In principle, two structures are possible for these redox resins: either the redox group is a substituent of a crosslinked polymer chain or it is a link itself in the polymer chain.

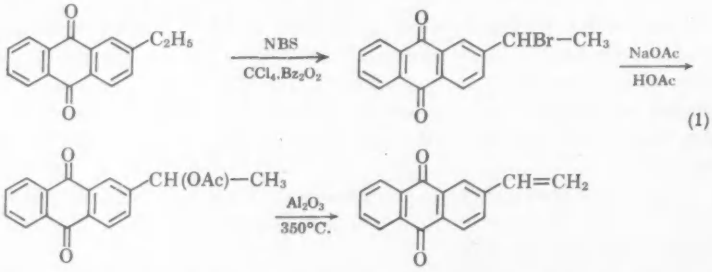
To the first class belong particularly the resins which were synthesized and investigated by Cassidy and co-workers;[1] these are based on vinylhydroquinone and its derivatives. Various representatives of the second class produced by polycondensation of different polyhydric phenols have been synthesized and investigated by us.[2] Both classes were tested mainly from two points of view. First, the stability and the reactivity were determined, and then their electrochemical properties were investigated. It was found that even in a medium pH region mild oxidizing agents caused irreversible oxidation and destruction of the resins. The rate of reaction, however, was usually reasonable. In order to increase the stability of the redox resins of both classes hydroquinones methylated in the nucleus were tried as components of the resins.[3–5] These resins are still under investigation. For polycondensation redox resins an attempt was also made to stabilize the hydroquinone system by using quinones or hydroquinones of the condensed aromatics.[6,7] The redox resins based on naphthoquinone and anthraquinone derivatives were indeed more chemically stable, but their reactivity was rather low.

In order to investigate the electrochemical properties of the redox resins of both types potentiometric titrations were performed. The following derivations from the comparable monomeric redox system were found: the midpoint potentials and the apparent standard oxidation-reduction potentials were more positive; the index potentials were greater, i.e. the titration curves were steeper. In both cases (polymerization and polycondensation redox resins) the redox resins contained at least two kinds of redox systems. In the polymerization redox resins the sulfonation was the

reason for the nonuniformity of the redox system, and with the polycondensation resins the polycondensation reaction itself was the cause for it.

In order to overcome these difficulties and to obtain a chemically stable redox resin we synthesized the 2-methyl-3-vinyl-1,4-naphthoquinone[8] and the 2-vinylanthraquinone;[9] the latter has also been synthesized by a different route by others, and some attempts at polymerization have also been reported.[10,11] The naphthoquinone derivative was not polymerizable, the corresponding hydroquinone diacetate polymerized only with great difficulty.

We therefore concentrated our efforts on the 2-vinylanthraquinone. Our synthesis was carried out by the route shown in eq. (1).



(1)

The 2-vinylanthraquinone so obtained is extremely pure. It polymerizes in solution and can be copolymerized with styrene and divinylbenzene very easily by radical mechanism. Because of the poor solubility of the monomer in common solvents (ca. 100 mg. 2-vinylanthraquinone/cc. at 100°C.), it seemed first that only resins with a very low capacity could be obtained by copolymerization. However, dimethyl sulfoxide was found to be a solvent which made possible thermal copolymerization of 2-vinylanthraquinone with styrene and divinylbenzene at 140°C. Up to 50 mole-% and more of 2-vinylanthraquinone could be copolymerized. When most of the dimethyl sulfoxide was replaced by *n*-butyl acetate and copolymerization was carried out at 100°C., redox polymers with a spongy structure were synthesized. After an exhausting extraction with methanol brittle yellow products were obtained. After swelling in dichloroethane a chlorosulfonation was performed in the same solvent at room temperature with chlorosulfonic acid. Saponification in warm water followed. For comparison it was checked whether under equal conditions 2-isopropylanthraquinone was sulfonated. Since it was found that no sulfonation of the anthraquinone took place, one can assume that also in the redox resins the anthraquinone system was not sulfonated.

In Table I are given the compositions, the ion-exchange capacities, and the redox capacities of the new redox resins. The ion exchange capacity could be easily determined in a reproducible way by salt splitting of 2*N* KCl by the oxidized form of the resin. The determination of the redox capacity could not be performed so easily. Because of the extremely high

TABLE I
Composition, Ion Exchange, and Redox Capacities of Sulfonated Poly-2-vinylanthraquinone Resins

Resin no.	Molar ratio of 2-vinylanthraquinone to sum of comonomers	DVB, mole-%	Ion exchange capacity, meq./g.		Redox capacity, meq./g.	
			Calcd.	Found	Calcd.	Found[a]
1	1:10 (spongy)	12.5	4.679	4.375	0.936	1.26
2	1:10	12.5	4.679	4.491	0.936	1.01
3	1:3	6.0	3.761	3.563	2.507	2.60
4	1:2	6.0	3.276	3.080	3.275	3.24
5	1:1	8.0	2.370	2.021	4.740	4.76
6	1:1	6.0	2.370	2.042	4.740	4.64
7	1:1	4.0	2.370	2.084	4.740	4.46

[a] Referred to an oxidation period of 60 days.

sensitivity of the reduced redox resins toward oxygen, prior to any determination they had to be reduced quantitatively with $NaBH_4$ in KOH under nitrogen. After acidification with H_2SO_4 a $0.05N$ Fe^{3+} solution in $2N$ H_2SO_4 was added, and the formed Fe^{2+} determined with permanganate.[12] As the redox capacity was well reproducible one can assume that under these conditions the redox resins were stable. The exact analysis of the determined values shows that the 2-vinylanthraquinone seems to be preferentially incorporated during the copolymerization.

A further characteristic property of redox resins is their oxidation–reduction potential. This was determined by potentiometric titration of the reduced form in $0.1N$ H_2SO_4 (pH 1.1–1.2) with $Ce(SO_4)_2$ solution. As a redox mediator small amounts of anthraquinone-2-sulfonic acid were added. Depending on the degree of oxidation and of the property of the redox resin, the times giving a constant reading ranged from 1 to 16 days after each addition of the titration solution. The reproducibility of the titration curves was good, although it was difficult to determine the endpoint of the titration and to establish an equilibrium state. The results are shown in Table II.

TABLE II
Apparent Standard Oxidation–Reduction Potentials and Index Potentials of Sulfonated Poly-2-vinylanthraquinone Resins

Resin no.	Apparent standard oxidation–reduction potential $E^{\circ}_{H^+}$, mv.	Index potential, mv.	
		$E_{50-25\ ox.}$	$E_{75-50\ ox.}$
1	179	17.5	18
1	177.5	14.3	14.5
2	178.25	16	16.3
2	178.5	14.5	14.8
5	191	18.5	18.5
5	192	23	22.5

All the redox resins synthesized with a low redox capacity, i.e. resins containing the anthraquinone in great dilution, exhibit a midpoint potential of +178 mv. (Fig. 1). The given potentials (in millivolts) are corrected to pH = 0 by the simple term $(RT/F) \ln [H^+] = -59.23$ pH. These potentials can therefore be called apparent standard oxidation–reduction potentials. A titration at pH 0 gave a consistent result.

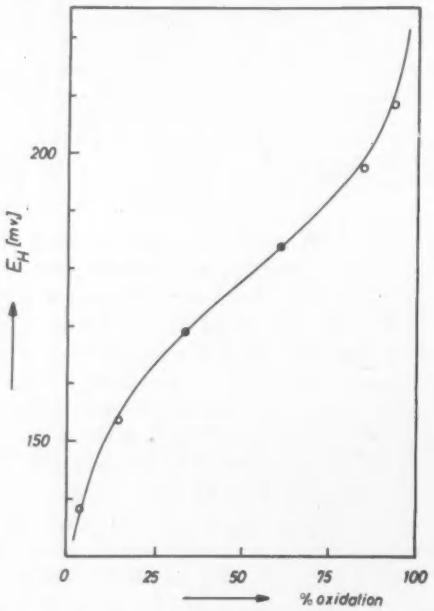


Fig. 1. A typical titration curve of a sulfonated poly-2-vinylanthraquinone resin (resin 1).

Resin 5, with the highest redox capacity, has a definite higher potential; its titration curve is also steeper. A direct comparison of the values obtained for the polymers with the oxidation reduction potentials of the comparable monomer, in this case the 2-isopropylanthraquinone, is not possible, as the monomer is insoluble in water.

As Josien et al.[13] pointed out, a relationship between the carbonyl stretching vibration frequency and the oxidation–reduction potential of quinones exists. We have, therefore, determined the oxidation–reduction potentials of some anthraquinones in acetic acid–water (1:1 v/v) and their C=O band in KBr. In Figure 2 it is clearly to be seen that also here this relationship exists. Water-soluble anthraquinone derivatives which have naturally a quite different solvation show this relationship only when oxidation–reduction potentials which were measured in water are taken into consideration. The values of the redox resins (measured in water) and

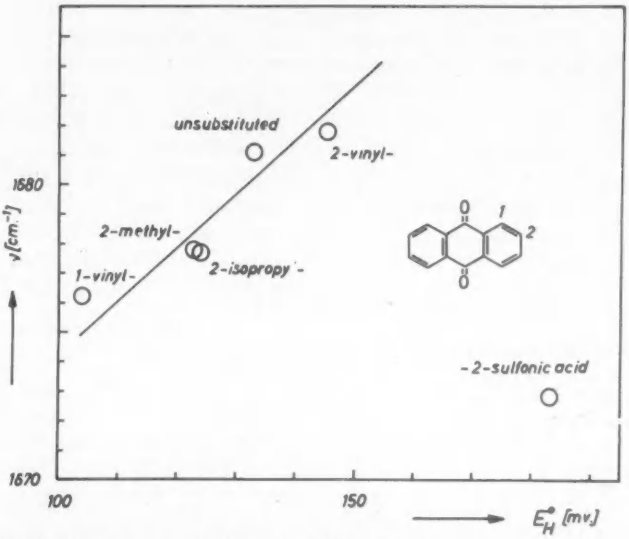


Fig. 2. Relationship between the C=O stretching vibration frequency and the standard redox potential of anthraquinones (measured in acetic acid–water).

the values of water-soluble anthraquinonesulfonic acids (taken from literature) do fit very well into this scheme (Fig. 3).

From Table III, showing the values for the C=O frequency, it can be seen that the absorption band of the 2-isopropylanthraquinone and the

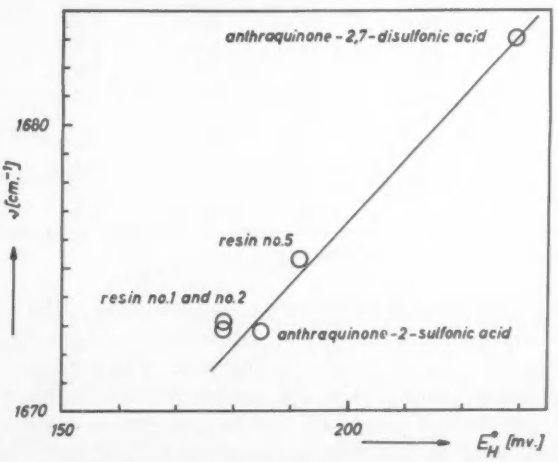


Fig. 3. Relationship between the C=O stretching vibration frequency and the redox potential of anthraquinones and sulfonated poly-2-vinylanthraquinone resins (measured in water).

TABLE III
C=O Stretching Vibration Frequency and Standard Redox Potentials of Anthraquinones and Poly-2-vinylanthraquinones

Substance	C=O frequency, cm.$^{-1}$	Standard oxidation–reduction potential E°_{H}, mv.
9,10-Anthraquinone	1681.1	133 (in HOAc–H_2O v/v)
2-Vinylanthraquinone	1681.8	146 "
2-Methylanthraquinone	1677.8	123 "
2-Isopropylanthraquinone	1677.7	124 "
1-Vinylanthraquinone	1676.2	104 "
Anthraquinone-2-sulfonic acid, Na salt	1672.8	183 "
		185 (in water[a])
Anthraquinone-2,7-disulfonic acid, di Na salt	1683.0	229 "
Poly-2-vinylanthraquinone	1678.4	
Resin 1 before sulfonation	1677.5	
Resin 5 before sulfonation	1677.8	
Resin 1, K salt	1673.1	178 (in water)
Resin 2, K salt	1672.8	178 "
Resin 5, K salt	1675.3	191.5 "

[a] Data of Clark.[15]

TABLE IV
Swelling Properties of Sulfonated Poly-2-vinylanthraquinone Resins

Resin no.	Weight-swelling, g. H_2O/g. dry resin[a]	Specific weight, g. dry resin/ml.	Specific volume, ml./g. dry resin	Ion exchange equivalent volume, ml./meq.	Redox equivalent volume, ml./meq.
1 oxd.	3.55_3	0.243	4.11_6	0.941	3.26_7
2 "	2.34_2	0.340	2.94_2	0.655	2.91_3
3 "	4.25_5	0.206	4.85_4	1.36_2	1.86_7
4 "	3.49_5	0.237	4.22_3	1.37_1	1.30_1
5 "	1.46_4	0.471	2.12_5	1.05_1	0.446
6 "	1.89_5	0.390	2.56_4	1.25_8	0.553
7 "	2.78_9	0.289	3.45_7	1.65_9	0.775
[5 red.	2.25_0	0.308	3.25	1.61	0.68]
[7 red.	3.80_9	0.225	4.45	2.14	1.00]

[a] Equilibrium solution: 0.5N H_2SO_4.

poly-2-vinylanthraquinone are almost at the same place. The copolymerization with styrene shifts the values only slightly, independently of the copolymerization ratio, to lower wave numbers. The sulfonated products show an additional clear shift of the band to the smaller wave numbers, and in this case the shift is dependent on the composition of the copolymer. The smallest value is exhibited by the redox resin with the highest ion exchange capacity (highest degree of sulfonation).

For the application of redox resins, not only a high redox capacity but also a reasonable rate of reaction is desirable. The redox resins described

here show this reasonable rate as long as no more than 70–80% of their total redox capacity is used.

The rate of reaction is surely a function of the swelling of the redox resins. Therefore, we investigate this dependence. The swelling measurements were carried out by the centrifuge method of Pepper et al.[14] on the fully oxidized redox resins. The results are shown in Table IV.

Analysis in these investigations proved that the new redox resins possess similar swelling properties as the cation-exchange resins based on styrene.

As the anthraquinone redox resins because of their low redox potential can be used only as reducing agents, we took as a measure of the reaction rate the time required for the reduction of a given amount of an oxidizing

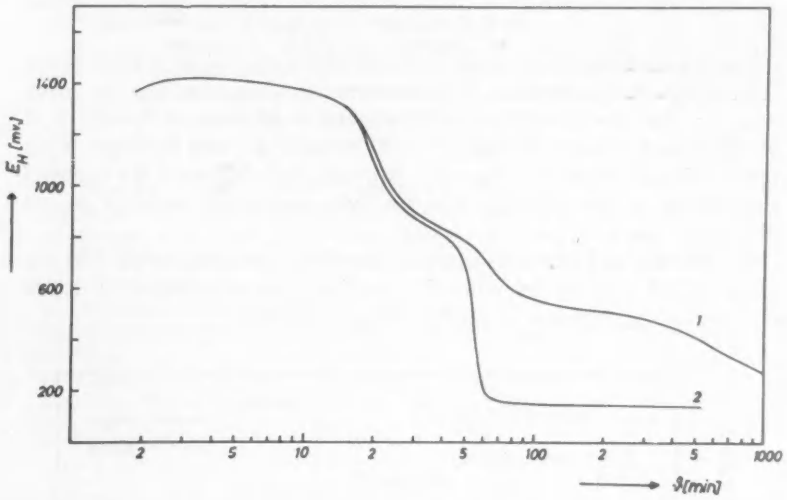


Fig. 4. Rate of reduction of Ce^{4+} solution by resin 1: (*1*) without mediator; (*2*) in presence of a mediator.

agent. The reaction rate of 0.50 meq. of the various redox resins in the reduced form (10% oxidized) suspended in 100 ml. of an aqueous solution was determined. This solution was $5 \times 10^{-4}N$ in Ce^{3+} and Ce^{4+} and $0.5N$ in H_2SO_4. The decrease of the potential with time was followed.

Figure 4 (curve 1) shows the decrease of the potential for resin 1 without a mediator and (curve *2*) the decrease for the same resin, but in the presence of a mediator. The influence of the mediator is observable only in the region of the potentials lower than 1300 mv. when already more than 99% of Ce^{4+} is reduced and especially strong in the region lower than 800 mv. At this potential the concentration of Ce^{4+} is about $10^{-14}N$ so that it is reasonable to assume that during further reduction the mediator gives the potentials of the electrodes. Table V indicates the times for the potential decrease up to 1300 and 1000 mv.

TABLE V
Times of Potential Decrease of a $5 \times 10^{-4}N$ Ce^{4+}/Ce^{3+} solution by Sulfonated Poly-2-vinylanthraquinone Resins

Resin no.	Potential of second inflecting point, mv.	Time, min.	
		1300 mv.	1000 mv.
1	850	15.2	22
2	850	18.5	26.25
3	810	26	38.5
4	820	39	55.5
5	800	170	218
6	800	80.5	108
7	820	33.5	45

The correlation of these values with the redox equivalent volume shows (Fig. 5) two characteristics. With redox resins of medium and low redox capacity, the rate of reaction is only slightly dependent on the degree of crosslinking, but more dependent on the redox equivalent volume. With redox resins of a high redox capacity, however, the influence of the degree of crosslinking is very strong, while the redox equivalent volumes do not differ very much.

In summary one can state that the rate of the reduction of Ce^{4+} by the redox resins is not only determined by the dimension of the pores (the degree of crosslinking), but also by their swelling conditions.

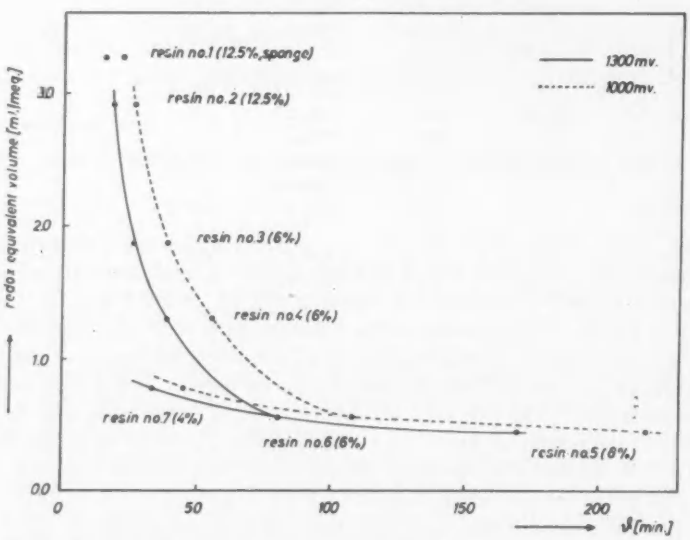


Fig. 5. Correlationship between the redox equivalent volume and the rate of reaction: (——) 1300 mv.; (– –) 1000 mv.

The spongy redox resin reacts quicker than the analogous normal redox resin. The rate of reaction up to ca. 50% oxidation is comparable with the rate of ion exchange processes in ion exchange resins.

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Synopsis

Polycondensation redox resins (electron exchange polymers) with *p*-quinone/hydroquinone redox groups show at the potentiometric titration in comparison with comparable monomer redox systems higher normal redox potentials and also raised index potentials. As the structure of the polycondensation redox resins is not uniform and as they are also chemically not very stable, new redox resins with uniform structure and better chemical properties were synthesized. For this purpose 2-methyl-3-vinyl-1,4-naphthoquinone and 2-vinyl-9,10-anthraquinone were synthesized. The naphthoquinone compound polymerized very badly. The new synthesis of the 2-vinylanthraquinone yielded a very pure monomer which showed very good polymerization and copolymerization-properties. A crosslinked copolymer of styrene, divinylbenzene, and 2-vinylanthraquinone was sulfonated. The so-produced swellable redox resins of relative uniform structure are resistant to mild oxidizing agents and chemically stable in all pH regions. The cation exchange capacity, the redox capacity, the normal redox potentials as well as the infrared-absorption were investigated as functions of the composition of the redox resins.

Résumé

Les résines de polycondensation rédox (échange d'électrons dans les polymères) avec des groupes redox *p*-quinone/hydroquinone, présentent à la titration potentiométrique,

en comparaison avec des systèmes rédox de monomères comparables, des potentiels rédox plus élevés que la normale, aisni que des index de potentiels plus élevés également. Comme la structure des résines de polycondensation rédox n'est plus uniforme et comme elles ne sont pas non plus chimiquement stables, on a synthétisé de nouvelles résines rédox possédant une structure uniforme et de meilleures propriétés chimiques. En effet, la 2-méthyl-3-vinyl-1,4-naphtoquinone et aussi la 2-vinyl-9,10-anthraquinone ont été synthétisées. La naphtoquinone polymérise très mal. La nouvelle synthèse de la 2-vinylanthraquinone donne un polymère très fin qui présente de très bonnes propriétés de polymérisation et de copolymérisation. On a sulfoné un copolymère ponté de styrène, divinylbenzène et 2-vinylanthraquinone. Les résines rédox ainsi produites, de structure relativement uniforme, sont résistantes envers les agents d'oxydation modérés et sont chimiquement stables dans toutes les régions de pH. On a étudié la capacité d'échange cationique, la capacité rédox ainsi que les potentiels rédox normaux, aussi bien que l'absorption IR en fonction de la composition de ces résines rédox.

Zusammenfassung

Polykondensations-Redoxharze (Elektronenaustauscher-Polymere) mit *p*-Chinon-Hydrochinon-Redoxgruppen zeigen bei der potentiometrischen Titration im Vergleich zu entsprechenden monomeren Redoxsystemen höhere Redox-Normalpotentiale und auch erhöhte Indexpotentiale. Da die Polykondensations-Redoxharze keine einheitliche Struktur besitzen und auch chemisch nicht sehr stabil sind, wurden neue Redoxharze mit einheitlicher Struktur und besseren chemischen Eigenschaften synthetisiert. Zu diesem Zweck wurden 2-Methyl-3-vinyl-1,4-naphthochinon und auch 2-Vinyl-9,10-anthrachinon dargestellt. Die Naphthochinonverbindung polymerisierte sehr schlecht. Die neue Synthese von 2-Vinylanthrachinon lieferte ein sehr reines Monomeres, das sehr gutes Polymerisations- und Copolymerisationsvermögen zeigte. Ein vernetztes Copolymeres aus Styrol, Divinylbenzol und 2-Vinylanthrachinon wurde sulfoniert. Die so gebildeten quellbaren Redoxharze mit verhältnismässig einheitlicher Struktur sind gegen milde Oxydationsmittel beständig und in allen pH-Bereichen chemisch stabil. Die Kationenaustauscherkapazität, die Redoxkapazität und auch Redoxnormalpotentiale sowie Infrarotabsorption wurden in Abhängigkeit von der Zusammensetzung der Redoxharze untersucht.

JOURNAL OF POLYMER SCIENCE: PART C NO. 4, PP. 1467–1480

Formation de Complexes Moleculaires sur hauts Polymères

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La formation de complexes polymériques par échange électronique a été étudiée sur la base d'analogies avec les systèmes organiques simples.

Dans une première orientation, on s'est basé sur les possibilités de fixation d'hydrocarbures aromatiques que présente le sulfocyanure de nickel lié à des dérivés pyridiniques ou à des amines arylalcoylées. Schaeffer[1] et Williams[2] ont attiré l'attention sur la séparation d'isomères aromatiques (par exemple le *p*-xylène) aux dépens de leur mélange au moyen de $Ni(SCN)_2(\gamma\text{-picoline})_4$. De même, plus récemment de Radzitsky et Hanotier[3] ont démontré que le sulfocyanure de nickel complexé à des amines arylalcoylées, telles l' α-méthylbenzylamine, est capable de former sélectivement des composés d'inclusion avec de nombreuses substances aromatiques, et que cette possibilité n'est pas seulement liée à la configuration spatiale mais également à la structure électronique des molécules aromatiques à inclure. Les sélectivités de complexation observées dépendent en effet du caractère électrodonneur ou électrocapteur des substituants des noyaux intéressés. Ces constatations suggèrent l'existence d'interaction π entre les noyaux aromatiques d'une part et le complexe sulfocyanure de nickel–amines d'autre part.

Sur la base de ces données, il était intéressant d'examiner également le comportement de complexes sulfocyanure de nickel–amine polymérique à l'égard de la fixation d'hydrocarbures aromatiques, et de comparer ce comportement à celui de complexes homologues simples. Par analogie avec le complexe de Schaeffer $Ni(SCN)_2(\gamma\text{-picoline})_4$ nous avons utilisé le complexe de sulfocyanure de nickel avec la poly-4-vinylpyridine atactique et isotactique et la poly-2-vinylpyridine isotactique.

Dans une seconde voie, nous nous sommes basés plus spécialement sur les échanges électroniques qui s'établissent entre des composés donneur et accepteur d' électrons entraînant la formation des complexes EDA (électrodonneur et accepteur). De nombreux complexes organiques de ce genre sont décrits et ont fait l'objet d'une monographie récente de Briegleb.[4]

Par contre, les propriétés d'échange électronique de substances polymériques n'ont été mentionnées, à notre connaissance, que récemment par Topchiev et ses collaborateurs[5] dans le cas des polymères et copolymères de la 2-méthyl-5-vinylpyridine en présence de dérivés nitrés aromatiques

(dinitrobenzène et dinitrotoluène). C'est dans ce sens que nous avons entrepris l'étude comparative de la complexation du dinitropolystyrène (électro-capteur) en présence d'amine aromatique (électrodonneur), et inversément la complexation de *p*-diméthylaminopolystyrène (électro-donneur) en présence de dérivés nitrés aromatiques (électrocapteurs); ces systèmes ont été comparés à des systèmes homologues de bas poids moléculaires.

1. Absorption d'Hydrocarbures Aromatiques sur Complexe (Sulfocyanure de Nickel–Poly-4-vinylpyridine), $Ni(SCN)_2(PVPy)_2$

La distance entre deux atomes d'azote pyridinique voisin d'une même chaîne de poly-4-vinylpyridine (PVPy) est trop élevée pour permettre l'établissement de deux liens de coordination avec un même sulfocyanure de nickel. En conséquence celui-ci forme un complexe à deux bases par pontage entre deux chaînes polymériques, les deux valences restées libres étant éventuellement occupées par le solvant au sein duquel a eu lieu la préparation (alcool amylique). Ces molécules de solvant (S) peuvent toutefois être aisément libérées par chauffage sous vide suivant l'équilibre

$$Ni(SCN)_2(PVPy)_2(S)_2 \rightleftarrows Ni(SCN)_2(PVPy)_2 + 2S$$

Il est donc à priori impossible d'assurer un arrangement spatial régulier indispensable à la formation de clathrate; l'inclusion d'hydrocarbure ou de dérivé étranger ne pourra résulter d'un piégeage au sein d'une cage cristalline, mais devra résulter de la complexation par l'étalissement d'une liaison π ou d'une liaison dative de coordination.

Afin de déterminer l'adsorption sélective des hydrocarbures sur les complexes macromoléculaires, l'adsorption à partir de différents mélanges d'hydrocarbures aliphatiques et aromatiques, d'hydrocarbures aromatiques mono- et bicycliques et d'hydrocarbures cyclo-aliphatiques, a été étudiée, par mise en suspension du complexe macromoléculaire dans le mélange d'hydrocarbure à étudier.

Les résultats obtenus ont été groupés dans le Tableau I. On y note, en regard de chaque mélange d'hydrocarbures, la composition du mélange initial et du liquide de désorption, la capacité en poids C_p, c.à.d. le poids d'hydrocarbures adsorbés par 100 g. de complexe, et les capcacités molaires C_m, c.à.d. le nombre de moles d'hydrocarbures adsorbées par mole de complexe.

L'examen du tableau I montre que le caractère aromatique de l'hydrocarbure joue un rôle important dans son adsorption sur le complexe polymérique, et que les hydrocarbures aliphatiques et cyclo-aliphatiques sont généralement moins adsorbés que les composés aromatiques.

La séparation sélective d'un mélange de deux hydrocarbures aromatiques est fonction de la richesse électronique du noyau des deux constituants; la séparation des constituants devenant d'autant plus laborieuse que la richesse électronique de leur noyau est équivalente. Ainsi qu'il faillait

s'y attendre, la tacticité de la chaîne n'exerce aucune influence sur le pouvoir d'absorption.

La capacité molaire est toujours relativement faible, et ne répond à aucune stoechiométrie; elle dépend de l'accessibilité des ions nickels au sein des résines et de l'encombrement des hydrocarbures.

TABLEAU I

Absorption d'Hydrocarbure Aromatique sur Complexe $Ni(SCN)_2(PVPy)_2$

Mélanges	% Initial	% Final	C_p	C_m	
1-Méthylnaphtalène–benzène	50:50	95:5	8.5	0.25	0.02
1-Méthylnaphtalène–*o*-xylène	49:51	60:40	14.8	0.28	0.22
1-Méthylnaphtalène–*p*-xylène	50:50	61:39	11.4	0.22	0.162
1-Méthylnaphtalène–sec-*n*-butyl-benzène	51:49	53:47	9.8	0.17	0.127
1-Méthylnaphtalène–tétraline	50:50	53:47	14.02	0.23	0.20
1-Méthylnaphtalène–1,2,4-Triméthyl benzène	49:51	55:45	10.4	0.184	0.154
p-Xylène–benzène	56:44	72:28	11.7	0.34	0.182
p-Xylène–toluène	51:49	58:42	10.8	0.253	0.211
———	51:49	58:42	10.4[a]		
p-Xylène–sec-*n*-butyl benzène	51:49	49:51	9.8	0.193	0.160
p-Xylène–isopropyl-benzène	52:48	49:51	10.3	0.205	0.188
p-Xylène–isopropyl-benzène	52:48	48:52	11.3[a]		
Benzène–hexane	50:50	77:23	7	0.316	0.064
Benzène–cyclohexane	50:50	51:49	9	0.268	0.212
Benzène–cyclohexane	49:51	59:41	8.4	0.287	0.164
Benzène–heptane	50:50	52:48	7.1	0.22	0.12
Toluène–Methyl cyclohexane	49:51	68:32	9.1	0.296	0.119
Toluène–heptane	49:51	80:20	6.1	0.237	0.04
Toluène–heptane	49:51	78:22	8[a]		
1-Methylnaphtalène–décaline	50:50	64:36	10.5	0.212	0.106
Tétraline–décaline	50:50	60:40	8.9	0.18	0.105
1-Méthylnaphtalène–2-méthylnaphtalène	56:44	55:45	14.8	0.248	0.2
o/*m*/*p*-Xylènes	33:31:36	31:29:40	14.3	0.183	−0.178 −0.225
Isooctane–heptane	51:49	48:52	8.5	0.155	0.188

[a] $(PVPY\ isotact.)_2\ Ni(SCN)_2$

Lorsque l'absorption des hydrocarbures sur les complexes macromoléculaires est effectué en présence d'alcools ou de phénol (Tableau II), on note une absorption largement préférentielle des composés hydroxylés; néanmoins la séparation des hydrocarbures aromatiques au départ de ces mélanges confirme les données du Tableau I.

TABLEAU II
Absorption d'Alcools et Hydrocarbures sur Complexe $Ni(SCN)_2(PVPy)_2$

Melanges	% Initial	% Final	C_p		C_m	
n-Butanol–heptane	53:47	94:6	15.2	0.81		0.03
	50:50	91:9	15.6	0.802		0.05
n-Butanol–*o,m,p*-xylènes	51:49	76:24	16.8	0.705		0.166
4-Méthyl-2-pentanol–toluène	55:45	72:28	9.3	0.382		0.177
4-Méthyl-2-pentanol–*o,m,p*-xylènes	53:47	58:42	20.3	0.47		0.346
Phénol–cumène	48:52	93:7	22.1	1.32		0.058
n-Butanol–toluène–hexane	34:33.5:32.5	88:10:2	10.2	0.498	0.049	0.008
n-butanol–toluène–cyclohexane	35:32:33	81:13:6	10.6	0.481	0.066	0.027
n-Butanol–toluène–*p*-xylène	35:33:32	80:8:12	10	0.446	0.038	0.051
n-Butanol–toluène–cumène	32:35:33	76:9:15	10.1	0.426	0.042	0.055
n-Butanol–décaline–tétraline	34:31:35	76:8:16	7.8	0.456	0.027	0.06
n-Butanol–1,2 Methyl-naphtalène	33:37:30	79:13:10	7.3	0.429	0.048	0.03
4-Méthyl-2-pentanol–toluène–heptane	36:32:32	70.5:22.5:5.7	7.9	0.226	0.089	0.019
4-Méthyl-2-pentanol–toluène–cumène	32:31:37	53:20:27	8	0.168	0.074	0.075
Benzyl alcool–toluène–*p*-xylène	34:33:33	81:8:11	9.8	0.318	0.028	0.037
Benzyl alcool–toluène cumène	26:37:37	78:10:12	11	0.338	0.042	0.039

La fixation des hydrocarbures aromatiques sur $Ni(SCN)_2(PVPy)_2$ est donc basée sur leur caractère électrodonneur; c'est le caractère plus basique des alcools qui entraîne leur déplacement au départ du complexe de nickel.

Il faut toutefois noter que l'absorption sur ces complexes polymériques est en premier lieu conditionnée par l'accessibilité des réactifs aux ions nickel du réseau polymérique; la basicité relative détermine uniquement le phénomène si les réactifs présentent un encombrement stérique équivalent. Cette constatation résulte directement des données du Tableau III.

Dans le cas des échanges (amines ou alcools) des volumes égaux des deux constituants ont été utilisés; dans le cas des amines ce mélange a été dilué à 20% dans l'heptane.

La capacité molaire est toujours la plus basse lorsque le site de coordination est encombré (comparaison des pyridine et picolines, des toluidines, de l'aniline et de la diméthylaniline, des butanols) indépendamment de la basicité du réactif; une séparation est toujours réalisée á l'avantage des amines et des alcools les moins volumineux.

Néanmoins, quoique la basicité des amines aliphatiques est nettement supérieure à celle des amines aromatiques (pK: n-butylamine, 3.38; pyridine, 8.85; aniline, 9.34) et que d'autre part le facteur stérique des amines et alcools aromatiques est fréquement plus important que le facteur stérique des produits aliphatiques, les amines et les alcools aromatiques sont préférentiellement adsorbés sur le complexe macromoléculaire par rapport

TABLEAU III

Fixation d'Amines (20% dans l'Heptane) et Alcools sur Complexe $Ni(SCN)_2$ $(PVPy)_2$

Amines	C_p	C_m		Alcool	C_p	C_m	
n-Butyl	34	1.9		Éthanol	(30)	(2.7)	
Diéthyl	16.8	0.96		n-Propanol	15.4	1.1	
Triéthyl	4.54	0.19		n-Butanol	14.24	0.8	
Pyridine	23.3	1.1		n-Pentanol	12.19	0.57	
α-Picoline	9.1	0.41		n-Hexanol	10.14	0.4	
γ-Picoline	23.2	1.04		4-Méthyl-2-pentanol	9.5	0.38	
Cyclohexyl	8.6	0.4					
Aniline	23.5	1.07					
o-Toluidine	8.7	0.34					
m-Toluidine	11.6	0.45					
p-Toluidine	13.6	0.53					
N,N-Diméthylaniline	7.9	0.3					
α-Méthylbenzylamine	15	0.5					
n-Butyl + diéthyl	22.2	0.94	0.3	n-Butanol + *tert*-butanol	12	0.48	0.19
n-Butyl + triéthyl	12.6	0.6	0.08	n-Butanol + 4-Méthyl-2-pentanol	12.8	0.49	0.144
Diéthyl + triéthyl	8.9	0.35	0.107	Isopentanol + 4-Méthyl-2-pentanol	13.5	0.38	0.221
Pyridine + α-picoline	12	0.52	0.08	n-Pentanol + 2-Méthyl pentanol	21.6	0.63	0.34
Pyridine + γ-picoline	30.7	0.87	0.61	n-Pentanol + 2-propyl-1-heptanol	13.6	0.51	0.07
α-Picoline + γ-picoline	10.4	0.06	0.4	n-Pentanol + cyclohexanol	11.1	0.35	0.16
Aniline + N,N-diméthylaniline	12.8	0.5	0.06				

aux amines et alcools aliphatiques. C'est ce qui ressort du Tableau IV relatif à des mélanges de dérivés aliphatiques et aromatiques.

Cette adsorption préférentielle des produits présentant un caractère aromatique pourrait s'expliquer par une interaction entre les noyaux aromatiques des produits adsorbés et les groupes pyridiniques de la chaîne macromoléculaire. Il ne nous a toutefois pas été possible de mettre cette interaction en évidence par spectrométries ultra-violette et infra-rouge, les

TABLEAU IV
Fixation Compétitive d'Amines et Alcools Aliphatiques et Aromatiques

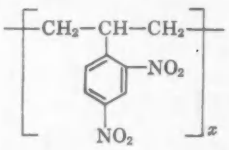
Mélanges	% Initial	%	C_p	C_m		
n-Butylamine–pyridine–heptane	10:10:80	44:54:1	33.8	0.71	1.09	0.02
n-Butylamine–aniline–heptane	10:10:80	41:58:1	34	0.66	1	0.005
Cyclohexylamine–aniline–heptane	10:10:80	18:81:1	20.7	0.13	0.78	0.005
Butanol–phénol–heptane	25:25:50	44:50:6	13.9	0.3	0.36	0.02
Cyclohexanol–phénol–heptane	25:25:50	43:52:5	25.5	0.45	0.65	0.03
	25:25:50	42:53:5	24	0.43	0.65	0.03
n-Butanol–benzyl alcool	50:50	38:62	22	0.40	0.59	
Cyclohexanol–benzyl alcool	50:50	44:56	10.7	0.20	0.24	

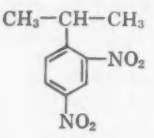
différences spectrales observées étant de l'ordre de grandeur de l'erreur expérimentale.

2. Formation de Complexes Électrodonneur–Accepteur (EDA)

On distingue généralement différents types de complexes EDA suivant la nature des donneurs et capteurs d'électrons intéressés à l'échange. Dans le travail que nous avons entrepris, nous nous sommes limités à la formation de complexes n–π, dans lesquels le donneur est une amine aromatique et l'accepteur un dérivé polynitré; on admet généralement que la formation des complexes est dans ce cas facilitée par la stabilisation par résonance des paires d'ions-radicaux formés.

Dans un premier cas, le 2,4-dinitropolystyrène (DNPStyr) a été complexé avec la α-naphthylamine (NA), et son comportement comparé à celui du 2,4-dinitrocumène (DNC), son homologue le plus simple:





Le choix s'est porté sur la α-naphtylamine, parce que cette amine présente une constante d'équilibre de complexation particulièrement élevée à l'égard de trinitrobenzene.[6,7]

L'étude spectrale a été effectuée dans les deux cas en présence de cyclohexanone comme diluant; les autres solvants du dinitropolystyrène ne conviennent pas à cause de leurs propriétés d'échange électronique. Dans les deux cas on observe dans le région visible du spectre une large bande d'absorption, fortement asymétrique, dont le maximum est situé à 410 mμ (DNC) et 430 mμ (DNPStyr.). La position de ces maxima est toutefois fonction de la concentration de la solution. Il se déplace vers les plus petites longueurs d'onde par dilution; au-delà de 0.035M de DNC on observe, malgré la dilution, une augmentation de l'intensité absorbée concomittament au déplacement vers les plus petites longueurs d'onde. La

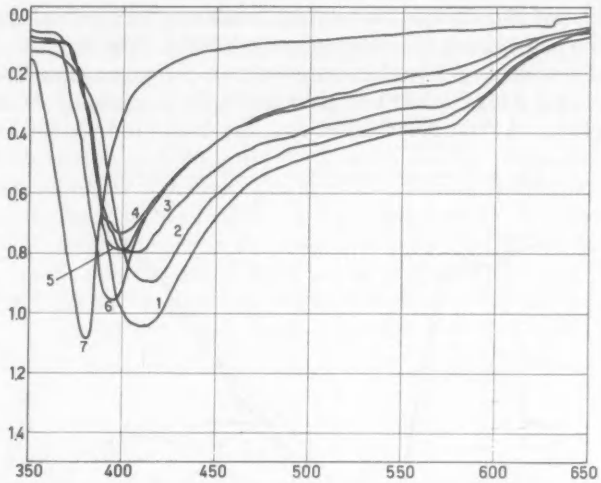


Fig. 1. Spectres d'absorption du système 2,4-dinitrocumène (DNC)–α-naphtylamine (NA): (*1*) DNC = 0.0533 mole/l., NA = 0.237 mole/l.; (*2*) DNC = 0.0480 mole/l.. NA = 0.212 mole/l.; (*3*) DNC = 0.0440 mole/l., NA = 0.197 mole/l.; (*4*) DNC = 0.0350 mole/l., NA = 0.157 mole/l.; (*5*) DNC = 0.0319 mole/l., NA = 0.142 mole/l.; (*6*) DNC = 0.0272 mole/l., NA = 0.111 mole/l.; (*7*) DNC = 0.0090 mole/l., NA = 0.037 mole/l.

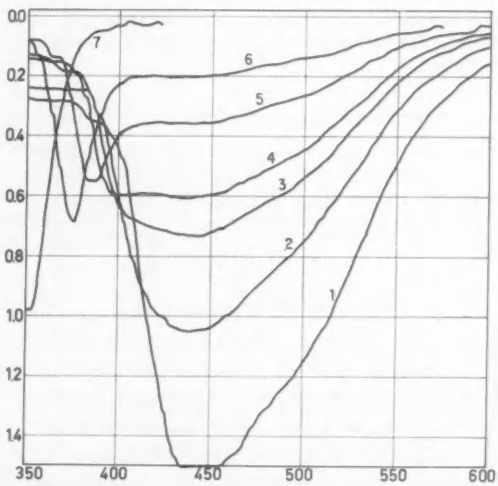


Fig. 2. Spectres d'absorption du mélange 2,4-dinitropolystyrène (DNPSt)–α-naphtylamine (NA): (*1*) DNPSt = 0.0693 mole/l., NA = 0.1843 mole/l.; (*2*) DNPSt = 0.0462 mole/l., NA = 0.1228 mole/l.; (*3*) DNPSt = 0.0347 mole/l., NA = 0.0921 mole/l.; (*4*) DNPSt = 0.0277 mole/l., NA = 0.0737 mole/l.; (*5*) DNPSt = 0.0174 mole/l., NA = 0.0461 mole/l.; (*6*) DNPSt = 0.0099 mole/l., NA = 0.0263 mole/l.; (*7*) DNPSt = 0.00113 mole/l., NA = 0.00302 mole/l.

bande devient plus étroite et à peu près symétrique; l'attribution de cette absorption nouvelle n'a toutefois pas pu être définie (Fig. 1).

Dans le cas du DNPSt la bande devient très fortement asymétrique par dilution; et à 0.01*M* DNPSt on peut déceler la présence de deux bandes d'absorption. A 0.0099*M* DNPSt λ_{max} est déjà située à 390 mμ. En

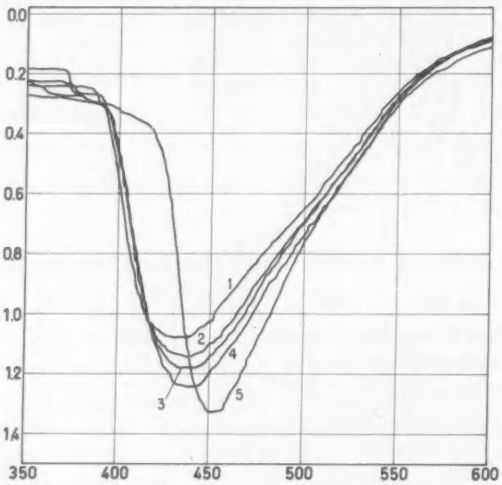


Fig. 3. Variation des spectres d'absorption de 2,4-dinitropolystyrène–α-naphtylamine en fonction du temps: (*1*) solution fraiche; (*2*) après 21 h; (*3*) après 45 h; (*4*) après 69 h; (*5*) après 36 jours.

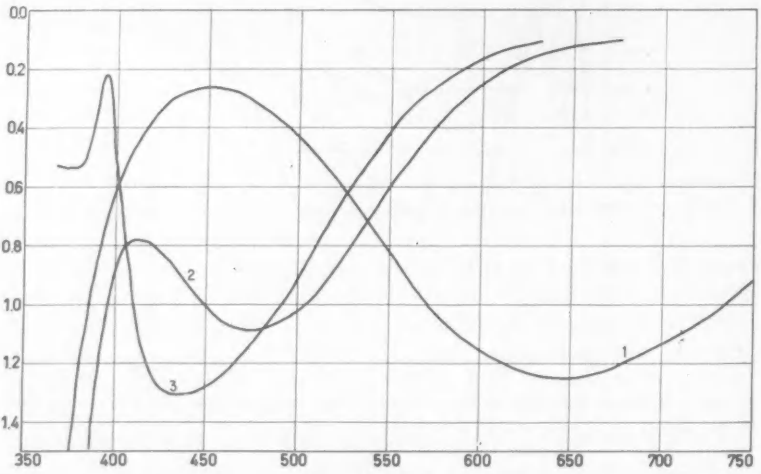


Fig. 4. Spectres d'absorption de (*1*) *N,N*-diméthylaniline (DMA) + chloranil, (*2*) DMA + trinitrobenzène, et (*3*) DMA + dinitrobenzène. Solvant: tétrachlorure de carbone.

outre on constate que la position exacte de λ_{max}, de même que son absorbance, augmentent légèrement en fonction du temps (Figs. 2 et 3).

Il est évident que, par suite de ces glissements de λ_{max}, l'évaluation de la constante d'équilibre de complexation devient très sujette à caution, sinon impossible.

L'asymétrie croissante de la bande d'absorption, de même que son déplacement suggèrent l'existence de deux ou plusieurs équilibres de complexation à stoechiométrie différente. La formation de complexe EDA suivie de réaction lente avec une autre molécule d'amine est également possible; elle a été suggérée dans le cas des complexes EDA du dinitrobenzène avec les amines primaires et secondaries[8].

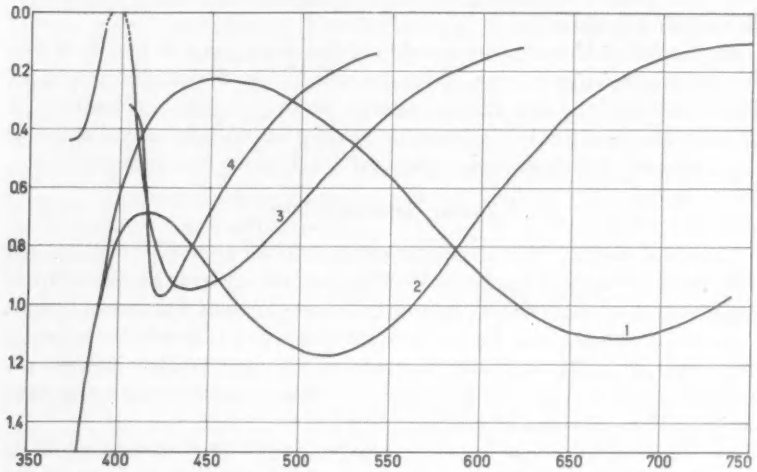


Fig. 5. Spectres d'absorption du *p*-diméthylaminopolystyrène en présence de (*1*) chloranil, (*2*) trinitrobenzène, (*3*) dinitrobenzène, et (*4*) nitrobenzène. Solvant: tétrachlorure de carbone.

Dans le second cas, le *p*-diméthylaminopolystyrène a été complexé en présence de divers accepteurs d'électrons, savoir le chloranil, le 1,3,5-trinitro-, 1,3-dinitro- et nitrobenzène. Le comportement a été comparé à celui de la *N,N*-diméthylaniline et de la *N,N*-diméthylcumidine (Figs. 4 et 5). Le polymère, de même que ses complexes EDA, est soluble dans le tétrachlorure de carbone et le chloroforme. Contrairement aux cas précédents, les complexes peuvent être préparés au départ de leur solution dans le tétrachlorure de carbone, et la position de maximum d'absorption reste fixe, indépendamment de la dilution. Dans ce cas-ci il est même aisé d'isoler les complexes d'addition par précipitation de la solution dans l'heptane. Partant la stoechiométrie des complexes peut être déterminée de même que les constantes d'équilibres correspondantes.

TABLEAU V
Complexes EDA de *p*-Diméthylaminé polystyrène et homologues: λ_{max}

Electrocapteur	Diméthylamino-polystyrene	Diméthyl: aniline	Diméthyl-cumidine
Chloranil	675 (bleu)	650 660 ($CHCl_3$)	665
Trinitrobenzène	525 (violet)	475	505
Dinitrobenzène	440 (brunrouge)	—	—
Nitrobenzène	425	—	—

La diminution des λ_{max} d'absorption correspond à l'électro-affinité décroissante des électrocapteurs; avec les dinitrobenzène et nitrobenzène il faut déjà tenir compte de l'absorption des composants libres en vue de définir les maxima (Tableau V).

En conclusion le comportement de polymères du point de vue de la formation de complexes EDA ne diffère que peu de celui des substances organiques homologues. Des déterminations de la constante d'équilibre à diverses températures permettront de calculer les enthalpies de formation dex complexes de même que les modifications d'entropie correspondantes.

Partie Experimentale

La poly-4-vinylpyridine a été préparée à 75°C au départ d'une solution à 30% dans le toluène en présence de 0.25% de peroxyde de benzoyle Après précipitation et purification, elle a été dissoute dans l'alcool butylique tertiaire, et obtenue sous forme de poudre blanche par lyophilisation de la solution. Les poly-4-vinylpyridine et poly-2-vinylpyridine isotactiques ont été préparés en présence d'organomagnésien comme initiateur suivant les indications de Natta et Mazzanti.[9]

Le nickel a été dosé par fixation au moyen de EDTA et titré en retour de l'excès de celui-ci par du nitrate de bismuth, en présence de pyrocatéchol violet.[10] Les dosages infra-rouges ont été effectués au moyen d'un spectromètre Perkin-Elmer à double faisceau modèle 21, les chromatographies gazeuses au moyen d'un Fractovap, Carlo Erba. Les courbes d'étalonnage ont été obtenues en mesurant les surfaces des pics enrégistrés à partir de mélanges de composition connue; les analyses ont nécessité suivant les cas des phases solides variées à différentes températures.

a. Structure du complexe polymérique $Ni(SCN)_2(PVPy)_2$. Les complexes polymériques forment un précipité gélatineux bleu-verdâtre dont on extrait l'alcool amylique par lavage au pentane; après sèchage sous vide à des températures de 30 à 150°C, ils se présentent sous la forme d'une poudre verdâtre. Bien qu'il se forme un précipité dès l'addition des premières gouttes de la solution de sulfocyanure, le polymère présente toujours une composition finale voisine du rapport stoechiométrique utilisé (7.8, 4 et 2.5 au lieu de 8, 4 et 2 respectivement).

Par sèchage sous vide du polymère et désorption fractionnée de l'alcool amylique, on peut démontrer que chaque atome de nickel est lié à deux

noyaux pyridiniques appartenant à différentes molécules du polymère, de même qu'à deux molécules d'alcool amylique; ces dernières ne peuvent pas être éliminées par lavage au pentane, uniquement par chauffage progressif de 30 à 150°C. Dans le cas de la poly-2-vinylpyridine, la structure du complexe polymérique est similaire. Un effet stérique considérable dû à la proximité de la chaîne polymérique empêche toutefois une fixation aussi élevée de nickel qu'avec la poly-4-vinylpyridine; en outre la formation de complexes intramoléculaires au départ d'un ion nickel et de deux azotes pyridiniques (*ortho*) voisins justifie une solubilité améliorée.

On peut évaluer que l'insolubilisation des chaînes polymériques provoquée par le sulfocyanure ou nickel entraîne l'isolement de 20% des noyaux pyridiniques du polymère entre les noyaux qui ont déjà réagi.

b. Absorption sur complexe $Ni(SCN)_2(PVPy)_2$. L'absorption des hydrocarbures a été effectuée à 25°C par mise en suspension du $Ni(SCN)_2$-$(PVPy)_2$ dans l'hydrocarbure ou le mélange d'hydrocarbures à envisager, p.ex. durant 3 jours. La capacité molaire croît rapidement au début du contact et atteint son palier asymptotique aprés environ 30 h; à 25°C elle ne varie pratiquement pas avec la température de contact, ni avec la méthode utilisée pour assurer le contact (suspension, filtration, précipitation). Après filtration, lavage rapide au pentane, les produits sont sèchés à l'air. Les hydrocarbures fixés sur le complexe polymérique sont désorbés sous vide à température croissante de 40–50°C à 150°C; ils sont recueillis dans une trappe plongeant dans l'air liquide. Leur composition a été déterminée soit par spectroscopie infra-rouge, soit par chromatographie gazeuse.

Les amines ont été absorbées au départ de solution à 20% dans l'heptane; la quantité d'amine correspond à un rapport molaire (amine/sulfocyanure Ni) = 3; la durée de contact était également de trois jours. L'absorption des alcools a été effectuée directement avec les alcools ou leur mélange. La rétention de l'heptane est toujours très faible; elle ne dépasse pas une capacité molaire de 0.03 et peut donc être négligée.

c. Le 2,4-dinitropolystyrène (DNPSt). Le 2,4-dinitropolystyrène (DNPSt) a été obtenue par initiation du polystyrène au moyen d'un mélange d'acides nitrique et sulfurique fumant. Il a été purifié par dissolution dans la cyclohexanone et précipitation dans du méthanol pur. La structure est démontrée par spectrométrie infrarouge; il contient 14.5% azote (théor. 14.43%). Au cours de la nitration la viscosité intrinsèque du polymère est réduite de moitié.

Les complexes EDA du dinitrocumène et du DNPSt ont été préparés par dissolution du dérivé nitré dans la naphthylamine fondue (3–4*M* amines pour 1*M* dérivé nitré). Après refroidissement le mélange est dissous dans la cyclohexanone et dilué jusqu'un volume déterminé. Les spectres ont été pris à un spectromètre Perkin-Elmer 137.

Le *p*-diméthylaminostyrène a été préparé par la méthode de Marvel.[11] L'aldéhyde benzoïque *p*-diméthylaminé est transformé en *p*-$Me_2NC_6H_4$-$CHOH$-CH_3 par réaction avec l'iodure de méthylmagnésium. Le carbinol

secondaire est déshydraté par distillation sous vide à 120°C. Ce monomère a été polymérisé en bloc à 70°C durant 12 h; après dilution au benzène, le polymère est précipité dans l'heptane. Il se présente sous forme d'une poudre blanche soluble dans le tétrachlorure de carbone et le chloroforme.

Contrairement aux cas précédents les complexes sont obtenus ici par mélange des deux solutions d'électrocapteur et électrodonneur dans le tétrachlorure de carbone.

Les auteurs remercient Labofina S.A. Bruxelles pour l'aide financière accordée au laboratoire de même que les bourses de recherches accordées à deux d'entr'eux (Y. C. et V.B.)

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Résumé

Le 2,4-dinitropolystyrène, obtenu par nitration du polystyrène, fournit des complexes EDA avec des hydrocarbures et amines naphtaléniques (α-naphtylamine). Similairement le polystyrène *p*-diméthylaminé lie les dinitro- et trinitrobenzène avec formation de paires de contact et de complexe. Le comportement des polymères est comparé à celui des homologues de bas poids moléculaire, tels le 2,4-dinitrocumène, et le cumène *p*-diméthylaminé. Les constantes d'équilibres de complexation sont comparées entr'elles et discutées. Leur évaluation spectrométrique est rendue difficile par le changement dans la position des maxima d'absorption et des coefficients d'absorption. De façon semblable, on a étudié le pouvoir d'absorption d'hydrocarbures à l'égard des complexes de coordination obtenus par addition de thiocyanate de nickel à la poly-4-vinylpyridine. Bien qu'il ne soit possible que d'obtenir un complexe de coordination à deux bases par ion-nickel, néanmoins la fixation d'hydrocarbures aromatiques est assez importante, et essentiellement fonction de la richesse électronique des différents noyaux aromatiques. Les hydrocarbures alphatiques ne sont que très faiblement adsorbés. L'adsorption d'alcools et amines a également été envisagée.

Synopsis

2,4-Dinitro polystyrene, obtained by nitration of polystyrene, gives EDA complexes with naphtalenic hydrocarbons and amines (α-naphtylamines). Similarly *p*-dimethylamino polystyrene binds dinitro- and trinitrobenzene with the formation of contact pairs and of complexes. The behavior of these polymers is compared to that of homologous low molecular weight substances as 2,4-dinitrocumene and *p*-dimethylaminocumene. The equilibrium constants of complex formation are compared with each other and discussed. Their spectrometric evaluation was difficult on account of a shift of the absorption maxima and a change of absorption coefficient. Similarly, the absorption power of hydrocarbons has been studied using coordination complexes of nickel thiocyanates with poly-4-vinylpyridine. Although it was not possible to obtain a coordination complex containing 2 pyridines for one nickel ion, nevertheless the fixation of aromatic hydrocarbons is appreciable, and mainly a function of the electron availability of the various aromatic nuclei. Contrarily aliphatic hydrocarbons are very poorly absorbed. The absorption of alcohols and amines has also been considered.

Zusammenfassung

Das durch Nitrierung von Polystyrol erhaltene 2,4-Dinitropolystyrol liefert mit Kohlenwasserstoffen und Naphthalin-Aminen (α-Naphthylamin) EDA-Komplexe. In ähnlicher Weise bindet das *p*-Dimethylamino-Polystyrol Nitro- und Trinitrobenzil unter Bildung von Kontaktpaaren und Komplexen. Das Verhalten der Polymeren wird mit dem von niedermolekularen Homologen, wie 2,4-Dinitrocumol und *p*-Dimethylaminocumol verglichen. Die Komplexbildungskonstanten werden untereinander verglichen und diskutiert. Ihre spektroskopische Bestimmung wird durch Änderungen der Lage und der Höhe der Absorptionsmaxima erschwert. In ähnlicher Weise wurde das Absorptionsvermögen der Kohlenwasserstoffe hinsichtlich der durch Addition von Nickelthiocyanat an Poly-4-vinylpyridin erhaltenen Koordinationskomplexe untersucht. Obwohl nur ein Koordinationskomplex mit zwei Basengruppen pro Nickelion erhalten werden kann, ist doch die Fixierung der aromatischen Kohlenwasserstoffe bedeutend genug und im wesentlichen eine Funktion des Elektronenreichtums der verschiedenen aromatischen Kerne. Die aliphatischen Kohlenwasserstoffe werden nur sehr schwach adsorbiert. Die Adsorption von Alkoholen und Aminen wurde ebenfalls in den Kreis der Betrachtungen gezogen.

Discussion

E. Selegny (*Faculté de Nantes, France*) [Il est évident qu'en anglais les initiales PTC, PAE, etc. . . s'inverseraient et donneraient CTP, EAP, etc. . . . comme toujours. (ex., RMN et NMR)]: (*1*) La préoccupation d'étudier les ressemblances et les différences entre les propriétés des polymères et de petites molécules organiques analogues, que vous venez de souligner dans votre communication, était également la nôtre depuis plus d'un diazine d'années.

C'est ainsi que nous avons préparé [E. Selegny, *Bull. Soc. Chim.*, pp. 1275–1289, 1281–1287, 1277, 1279, 1286, et 1287 (1959)] une série de polymères pourvus de fonctions azotés aromatiques, soit par polymérisations soit encore par polycondensations formophénoliques; entre autres le poly-(*p*. *N*-diméthylaminostyrène) (ou DAS) (1 bis) et les produits de polycondensation dû *p*. *N*-diméthylaminophénol et de l'ammonium quaternaire correspondant (1 *cis*).

Ce sont les propriétés particulières de ce dernier vis-à-vis d'ions chlorure et nitrate [E. Selegny, *Bull. Soc. Chim.*, 1303, 1304 (1959)] et du DAS vis-a-vis de l'oxygène [E. Selegny, *Bull. Soc. Chim.*, pp. 1287 (1959)] qui nous ont mis sur la piste des complexes par transfert de charge des polymères; par ailleurs, certains de nos complexes sont d'un nouveau type.

Nous avons pu depuis confirmer par diverses méthodes électrochimiques [D. L. Trang, S. Morazzani-Pelletier, and E. Selegny, Angers le 15.12.62; *Bull. Soc. Chim.*, p. 1137 (1960)] l'exactitude de notre point de vue et nous sommes depuis quelques temps en possession des constantes des complexes qui seront détaillées dans un prochain travail (D. L. Trang, Thèse de 3 ème cycle de en reduction, Paris). Nous avons egalement rapporté déjà un nouveau cas semblable [E. Selegny et. Mme. M. Lancon (Angers 15.12.62), *Bull. Soc. Chim.*, p. 1137 (1963)].

Par ces premiers exemples nous avons en quelque sorte parcouru, à l'aide d'ions minéraux, un chemin inverse (puisque partis de polymères), mais parallèle à vos travaux. Des résultats plus récents nous laissent constater (E. Selegny et Y. Merls, "Calculs d'équilibres d'echanges d'ions. III. Verifications experimentales," a paraître) que le DAS se comporte d'une manière analogue dans certaines circonstances pas seulement avec l'oxygène mais encore avec les ions d'halogènes. De même nous avons indiqué [D. L. Trang, S. Morazzani-Pelletier, and E. Selegny (Angers le 15.12.62) et *Bull. Soc. Chim.*; p. 1137 (1963)] que nous poursuivions et élargissions [E. Selegny, *Bull. Soc. Chim.*, p. 1137 (1963); conférence à le Faculté des Sciences de Paris (Bûtiment P) le 6-63; communications privée avec le Prof. Wiemann (Fac. Sci., Paris, même date)] le champ de ces investigations.

(*II*) En outre nous avons déjà pensé qu'il conviendrait d'appeler polymères echangeurs de ligands (PEL) au moins les polymères renfermant un métal, car les absorbats y sont associés effectivement sous la forme de ligandes.

Plus généralement tous ces polymères de transfert de charge (PTC) pourraient se subdiviser en polymères donneurs l'électrons (PDE) et accepteurs d'électrons (PAE).

J'appelerais en outre de premier type les PTC agissant intrinsèquement (PTC-1) mais de deuxième type (PTC-2) ceux qui opèrent grâce à un ion ou un composé retenus, comme par exemple les échangeurs de ligandes (PEL).

Ces conventions permettraient d'introduire un peu d'ordre dans la classification des préparations usitées par exemple par des analystes et qu'il serait fastidieux d'énumérer (voir par exemple l'ouvrage de O. Samuelson).

(*III*) Quantativement les propriétés préférentielles ou sélectives se caractérisent encore le mieux par des constantes, telles que K_1 = constante de *formation* de ligande et K_{DA} = constante de formation donneur-accepteur ou plus généralement de K_{TC} = constante de formation de complexe par transfert de charge—analogues à celles usitées pour les échangeurs d'ions—et dont le rapport pour deux cas différents peut donner la constante de séparation.

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New Ferrous-Containing Polymers Based on Ferrocene and Their Electrophysical Properties

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At the present time quite a few polymers based on ferrocene and its derivatives are known.

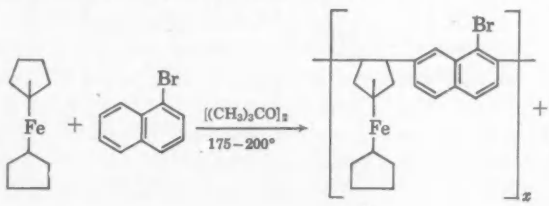
In 1955 there were prepared polymers of vinylferrocene and its copolymers with methyl methacrylate, styrene, and chlorobutadiene[1,2] containing branch ferrocene rings. Knobloch and Rauscher[2] have prepared polymers containing ferrocene rings in the main chain by polycondensation of chloric anhydride 1,1′-dicarboxyferrocenic acid with diamines (ethylenediamine, hexamethylenediamine, diethylenediamine, *p*-phenylenediamine) and with dioxy compounds (4,4′-isopropylenediphenol, hydroquinone).

From the interaction of ferrocene and methylene chloride and 1,2-dichloroethane in the presence of aluminum chloride Nesmeyanov et al.[3] have obtained solid polymers. From the reaction of polyrecombination[3–6] of ferrocene and diisopropyl ferrocene there were obtained soluble (linear) and insoluble polyferrocenylenes with molecular weights from 1000 up to 7000 and polydiisopropylferrocenylene with molecular weight 8000.

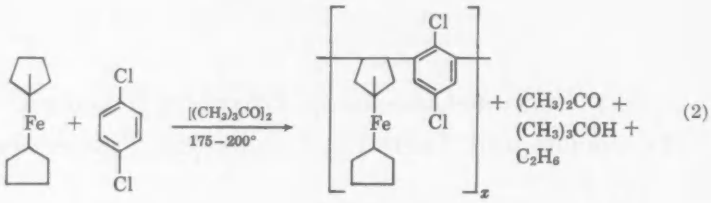
The authors have prepared a number of new polymers on the basis of ferrocene and have studied their properties.[7]

From the polyrecombination reaction of ferrocene with a number of aromatic compounds (α-naphthalene bromide, *p*-dichlorobenzene, salicylic acid, salicylaldehyde, and benzaldehyde) at ~175–200° in the presence of *tert*-butyl peroxide with various reactant-to-peroxide molar ratios the yield is 3–39% of soluble (dark brown) polymers and 23–77% of insoluble (black, solid) polymers.

The formation of soluble polymers in the reaction of polyrecombination can be indicated by the eqs. (1) and (2):



(1)

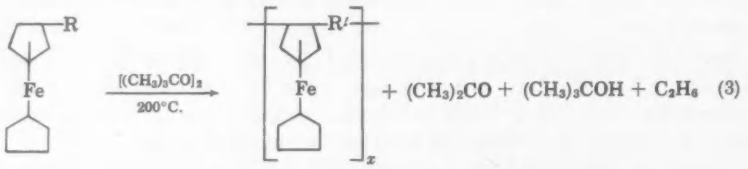


(2)

The molecular weights of the soluble polymers are within the range of 2000–3000; the elementary composition and Fe content are in good agreement with the assumed structure.

The insoluble polymers have the three-dimensional network type of structure; they are infusible up to 500°C.

The polyrecombination of alkyl ferrocenes (i-$C_4H_9C_5H_4FeC_5H_5$, i-C_5H_{11}-$C_5H_4FeC_5H_5$, and i-$C_8H_{17}C_5H_4FeC_5H_5$) gives only soluble polymers (light brown), melting at 280–300°C.:

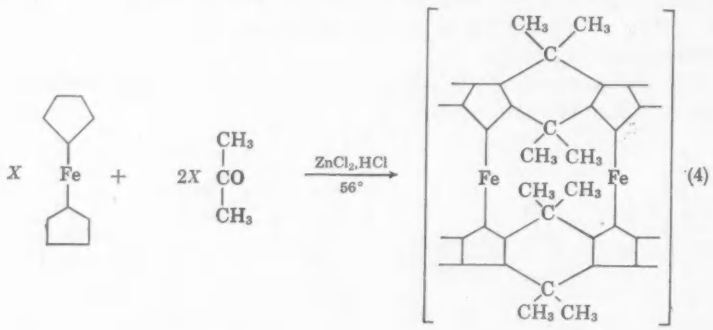


(3)

where R is i-C_4H_9. i-C_5H_{11}, and i-C_8H_{17}. Characteristics of the polymers are given in Table I.

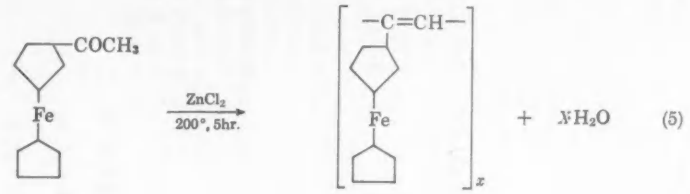
By the polycondensation reaction we have obtained new ferrocene-containing polymers based on ferrocene and acetone, acetyl ferrocene, and 1,1′-diacetylferrocene.

By polycondensation with acetone in the presence of $ZnCl_2$ and hydrogen chloride, ferrocene forms soluble high molecular compounds (unlike benzene and its homologs) with molecular weight 3000–3200 and melting point 320–360°C., as shown in eq. (4).

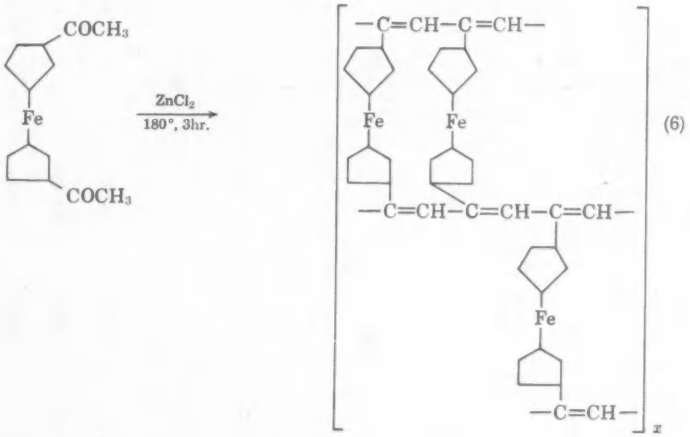


(4)

Polycondensation of acetyl and 1,1′-diacetylferrocenes forms both soluble and insoluble polymers:



(5)



(6)

Characteristics of these polymers are given in Table II.

The prepared polymers (except polyisobutylferrocene) produce a one-component signal in the ESR spectrum; according to the x-ray data the polymers are amorphous. The infrared absorption spectra of the polymers (recorded by an IKS-14 spectrophotometer) show that all the soluble specimens have absorption bands characteristic of ferrocene compounds.[8] A strong absorption band at 816 cm.$^{-1}$ corresponding to out-of-plane deformation vibrations of the C—H group in the ferrocene ring, clear absorption bands at 1000, 1100, and 1104 cm.$^{-1}$ corresponding to the vibrations of the hydrogen atoms remaining on the cyclopentadienyl ring of ferrocene, a broad band of absorption in the 1640–1650 cm.$^{-1}$ region (but without a clearly indicated maximum), and also a weak absorption band in the 3030–3080 cm.$^{-1}$ region caused by the valent vibrations are found. In the spectra of the copolymers of ferrocene α-naphthalene bromide, and p-dichlorobenzene there are observed rather sharp absorption bands characteristic of the C—Br bond (675 cm.$^{-1}$), the position specific for α-naphthalene bromide and C—Cl bond (678 cm.$^{-1}$), and also a number of absorption bands characteristic of the naphthalene ring and benzene ring.[9]

TABLE I. Characteristics of Fe-Containing Polymers Obtained by Polyrecombination at 175–200°C.

No.	Reactants	Molar ratio peroxide: reactants	Polymer yield (based on reactants), wt.-%		Molecular weight of soluble polymer	Melting point, °C.		Analytical data (found, %)	
			Soluble polymer	Insoluble polymer		Soluble polymer	Insoluble polymer	Soluble polymer	Insoluble polymer
1	Ferrocene + α-naphthalene bromide	1.36:1	5.4	23.0	2270–3000	>500	>500		
2	"	3:1	6.6	26.8	—			C 63, H 4.44, Br 19.96, Fe 12.03[a]	C 62.56, H 4.37, Br 17.93, Fe 15.14
3	Ferrocene + p-dichlorobenzene	1.6:1	5.2	23.0	1200				
4	"	3:1	4.1	32.9	—	>500	>500	C 62.92, H 5.21, Cl 11.65, Fe 20.22	C 60.83, H 4.82, Cl 11.10, Fe 23.25
5	Ferrocene + benzonitrile	2:1	None	27	—	—	>500	—	C 74.36, H 6.09, N 3.97, Fe 19.28
6	Ferrocene + salicylicacid	1.8:1	None	77	—	—	>500	—	C 63.66, H 4.26, Fe 17.17, O 14.91
7	Ferrocene + salicylaldehyde	1.5:1	3.3	35.7	—		>500	—	C 69.94, H 4.48, Fe 18.16, O 7.42
8	Ferrocene + benzaldehyde	2:1	—	—	—		>500	—	C 78.29, H 5.43, Fe 19.1, O 10.28
9	Monoisobutylferrocene	2:1	39	None	2300	300	—	C 68.42, H 6.80, Fe 24.76[b]	—
10	Monoisoamylferrocene	2:1	35.5	None	1300	290–295	—	C 69.77, H 7.17, Fe 23.06[c]	—
11	Monoisooctylferrocene	2:1	34	None	2000	290	—	C 73.37, H 8.11, Fe 18.52[d]	—

[a] Calculated for $C_{20}H_{13}FeBr_2$: C 61.7%, H 3.3%, Br 20.4%, Fe 14.4%. [b] Calculated for $C_{14}H_{18}Fe$: C 70.00%, H 6.67%, Fe 23.38%. [c] Calculated for $C_{15}H_{18}Fe$: C 71.00%, H 7.10%, Fe 21.90%. [d] Calculated for $C_{18}H_{24}Fe$: C 73%, H 8%, Fe 19%.

[a] Calculated for $C_{20}H_{18}FeBr_2$: C 61.7%, H 3.3%, Br 20.4%, Fe 14.4%. [b] Calculated for $C_{15}H_{18}Fe$: C 71.00%, H 7.10%, Fe 21.90%. [c] Calculated for $C_{18}H_{24}Fe$: C 73%, H 8%, Fe 19%.

TABLE II
Characteristics of Fe-Containing Polymers Obtained by Polycondensation

No.	Reactants	Conditions of Reaction	Polymer yield, wt.-%		Molecular weight of soluble polymer	Melting point, °C.		Analytical data (found, %)	
			Soluble polymer	Insoluble polymer		Soluble polymer	Insoluble polymer	Soluble polymer	Insoluble polymer
1	Ferrocene (F) + acetone (A)	F:4:$ZnCl_2$ = 0.1:2:0.03	53.8	None	3000–3200	320–360	—	C 75.73, H 7.6, Fe 16.0[a]	—
2	Acetylferrocene (AF)	AF:$ZnCl_2$ = 1:036, 200°C., 5 hr.	19.5	74.8	3600	210–270	>500	—	C 69.9, H 6.5, Fe 21.1
3	Diacetylferrocene (DAF)	DAF:$ZnCl_2$ = 2.38:1, 180°C., 3 hr.	None	90	—	—	>500	—	C 66.16, H 4.68, Fe 24.1

[a] Calculated for $C_{22}H_{26}Fe$: C 76.20%, H 7.4%, Fe 16.1%.

In the spectra of polyrecombination products of alkylferrocenes there are absorption bands in the 1380 and 1460–1480 cm.$^{-1}$ regions which correspond to the C—H deformation vibrations in the aliphatic chains and the stretching vibrations in the methyl and methylene groups in the 2970–2928 cm.$^{-1}$ region.

For the insoluble polymers in the infrared spectra (copolymers of ferrocene with α-naphthalene bromide (Fig. 1) and p-dichlorobenzene (Fig. 2)

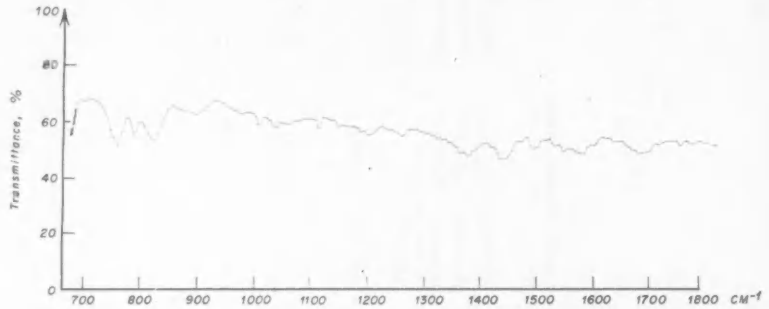


Fig. 1. Infrared absorption spectrum of insoluble copolymer of ferrocene and α-naphthalene bromide. Ordinate: transmittance, %.

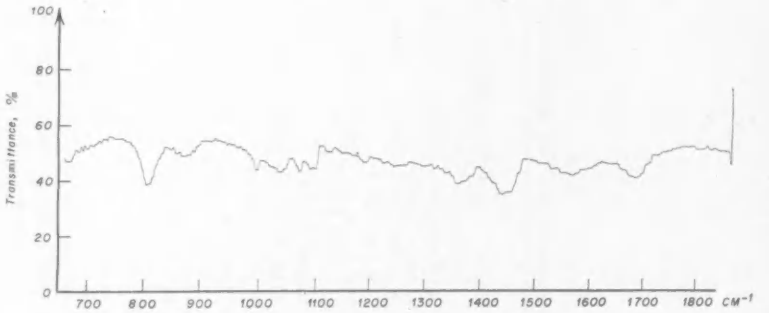


Fig. 2. Infrared absorption spectrum of insoluble copolymer of ferrocene and p-dichlorozene. Ordinate: transmittance, %.

there is observed a considerable increase of the absorption background together with simultaneous flattening of certain absorption bands.

The infrared spectrum of the polymer of 1,1′-diacetylferrocene (Fig. 3), which at a concentration of 0.5 mg. of the polymer for 250 mg. KBr, shows considerable absorption (60%) with the complete flattening of certain absorption bands as is characteristic of polyconjugated polymer systems which can have semiconductive properties.[10–12] We have studied the electrophysical properties of the prepared polymers.

TABLE III
Electrophysical Properties of the Prepared Polymers

No.	Polymer	Ratio of reactants: *tert*-butyl peroxide	E, e.v.	δ_{20}, ohm^{-1}cm.$^{-1}$
1	Copolymer of ferrocene and α-naphthalene bromide (soluble)	1:1.36	1.74	1.35×10^{-20}
2	" (insoluble)	1:1.36	0.54	2.5×10^{-13}
3	" (insoluble)	1:3	0.54	1.7×10^{-13}
4	Copolymer of ferrocene and *p*-dichlorobenzene (insoluble)	1:1.6	0.47	2.83×10^{-10}
5	" (insoluble)	1:1.8	0.30	8.86×10^{-12}
6	" (insoluble)	1:2.5	0.38	1.55×10^{-10}
7	" (insoluble)	1:3	0.58	2.5×10^{-12}
8	Copolymer of ferrocene and salicylic acid (insoluble)	1:1.8	0.33	4×10^{-9}
9	Copolymer of ferrocene and salicyl aldehyde (insoluble)	1:1.5	0.45	3.7×10^{-12}
10	Polyiso butylferrocenilene (soluble)	1:2	0.83	1.5×10^{-15}
11	Polymer of ferrocene and acetone (soluble)	—	0.67	1.23×10^{-12}
12	Acetylferrocene polymer (insoluble)	—	1.45	2.8×10^{-10}
13	1,1′-Diacetylferrocene polymer (insoluble)	—	0.42	2.36×10^{-11}

The method of measurement of conduction dependence on temperature described,[7] enabled us to make measurements under pressure of 5×10^{-5} mm. Hg and within the temperature range 20–300°C.

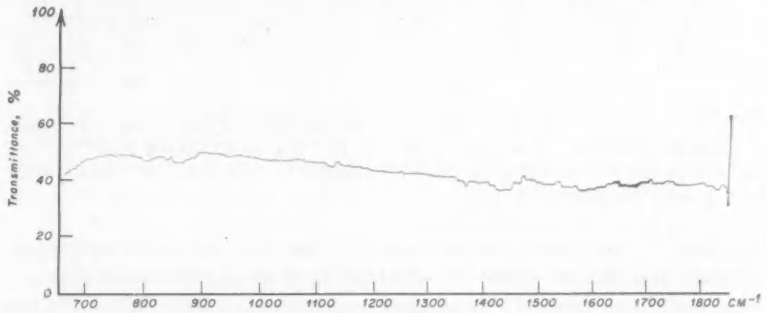


Fig. 3. Infrared absorption spectrum of insoluble polymer of diacetylferrocene. Ordinate: transmittance, %.

In order to remove from the specimen comparatively easy desorbable substances (gases, water vapor, etc.) the pellets before each measurement were kept under pressure of 1×10^{-4} mm. Hg for 3 hr. at 50°C.

In Table III there are given activation energies E and conductance at 50°C. (σ_{50}) of the prepared polymers. All the specimens have a positive

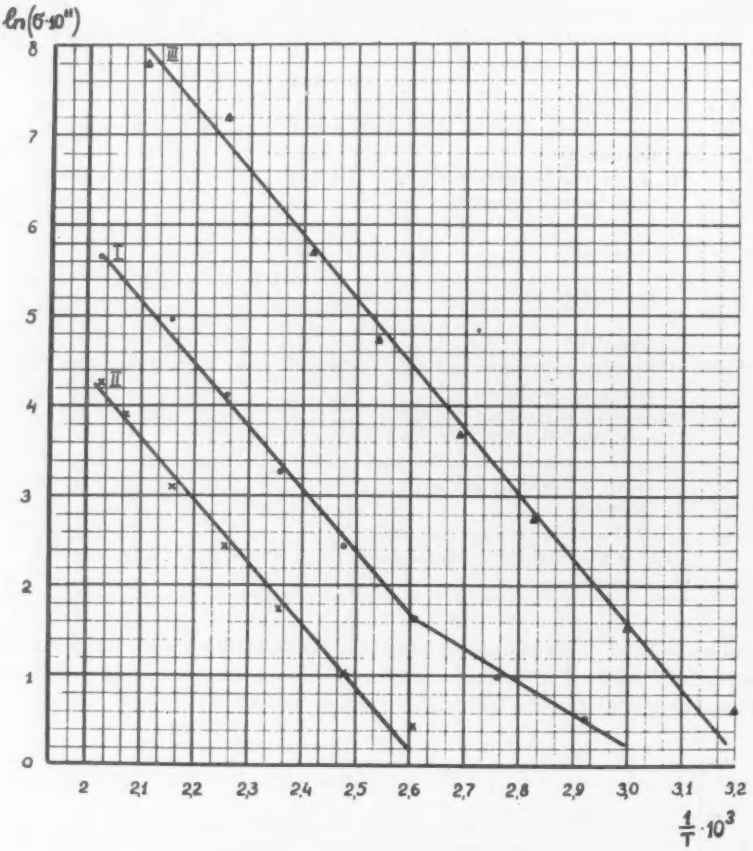


Fig. 4. Conduction dependence on temperature for insoluble copolymer of ferrocene and *p*-dichlorobenzene: (*1*) $\sigma = \sigma(T)$, at 1×10^{-4} mm. after heating to 50°C.; (*2*) $\sigma = \sigma(T)$ at 1×10^{-4} mm. after heating to 50 and 220°C.; (*3*) $\sigma = \sigma(T)$ at 760 mm. after heating to 50, 220, and 220°C.

temperature coefficient of conduction and the temperature dependence of conduction within the studied range of temperatures is exponential (Fig. 4).

As seen from Table III the studied semiconductive materials under the above described conditions of measurement have an activation energy of 0.3–1.74 e.v. (for most of the specimens $E \simeq 0.4$ e.v.) and specific electro-

TABLE IV
Influence of Pretreatment Conditions and Conditions of Measurement on σ and E

Polymer	Pretreatment conditions: Duration, hr.	Pretreatment conditions: Temp., °C.	Pretreatment conditions: Pressure, mm. Hg.	Pressure at measurement, mm. Hg	σ, ohm^{-1}cm^{-1}.	E, e.v.
Ferrocene α-naphthalene bromide (insoluble)	3	50	1×10^{-4}	1×10^{-4}	2.5×10^{-13}	3.62 0.54
"	3	200	1×10^{-4}	760	5.4×10^{-8}	0.32
Ferrocene + acetone (soluble)	3	50	1×10^{-4}	1×10^{-4}	1.23×10^{-12}	0.67
"	3	200	1×10^{-4}	1×10^{-4}	6.2×10^{-14}	1.13
"	3	200	1×10^{-4}	760	9.2×10^{-11}	0.68
Acetylferrocene (insoluble)	3	50	1×10^{-4}	1×10^{-4}	2.85×10^{-10}	1.45 0.47
"	3	20	1×10^{-4}	760	1.0×10^{-9}	0.47 0.31
Ferrocene + salicylic acid	3	50	1×10^{-4}	1×10^{-4}	4×10^{-9}	0.33
"	3	200	1×10^{-4}	1×10^{-4}	4.22×10^{-10}	0.34 0.53
"	3	200	1×10^{-4}	760	9.53×10^{-9}	0.45
1,1′-Diacetylferrocene	3	50	1×10^{-4}	1×10^{-4}	2.36×10^{-11}	0.42 1.4
"	3	300	1×10^{-4}	1×10^{-4}	5.9×10^{-8}	0.05
"	3	300	1×10^{-4}	1×10^{-4}	8.85×10^{-7}	0.2

conductivity at 50°C. at 1×10^{-20}–4×10^{-9} ohm^{-1} cm.$^{-1}$ (for most of the specimens $\sigma_{50} \simeq 10^{-10}$–$10^{-12}$ ohm^{-1} cm.$^{-1}$).

Electric conduction of an insoluble copolymer of ferrocene and α-naphthalene bromide is 7 orders higher and the activation energy is 3 times less than for a soluble copolymer of ferrocene and α-naphthalene bromide. As a rule the insoluble specimens of the polymers have greater molecular weight than the soluble ones. It is possible that conduction of these polymers is mainly connected with "contacts" between macromolecules which results in the influence of the molecular weight on the electrophysical properties.

All the studied polymers have rather high electric resistance; better electrophysical properties are exhibited by the copolymer of ferrocene and salicylic acid and the polymer of 1,1′-diacetylferrocene.

The observed conduction of polymer semiconductors with a system of conjugated bonds, to which, according to the data of the infrared absorption spectrum, 1,1′-diacetylferrocene (Fig. 3) and its analogs belong, depends considerably on absorption of their surface[14] (as in case of ordinary semiconductors). We have studied the electrophysical properties of the prepared polymers under various degrees of desorption. The correspond-

ing data are given in Table IV, where the conditions of the pretreatment are indicated as well as the conditions of measurement.

As seen from Table IV the heating of the specimens under 1×10^{-4} mm. Hg for 3 hr. leads to a decrease of electric conduction of the polymer (and in certain cases to a decrease of the activation energy). The consequent adsorption from the air (under 760 mm. Hg) leads to an increase of conduction (1–5 orders) and to some decrease of the activation energy.

The most pronounced effect of σ decrease is displayed by the copoly-

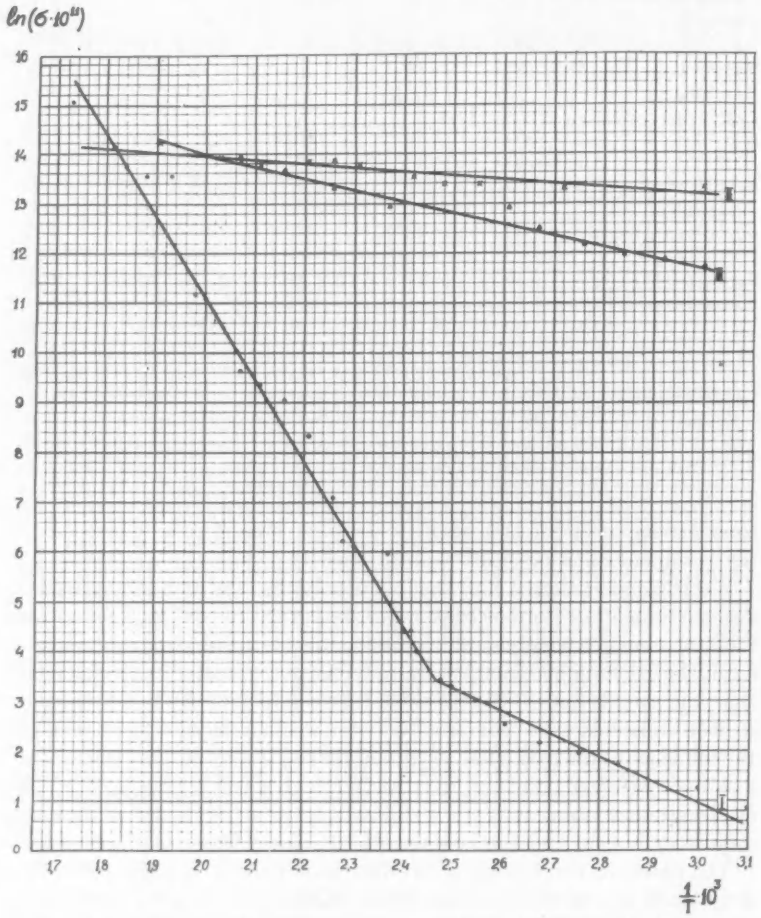


Fig. 5. Conduction dependence on temperature for insoluble polymer of diacetylferrocene: (*1*) $\sigma = \sigma(T)$ at 1×10^{-4} mm. after heating to 50°C.: (*2*) $\sigma = \sigma(T)$ at 1×10^{-4} mm. after heating to 50, 300, and 300°C.; (*3*) $\sigma = \sigma(T)$ at 1×10^{-4} mm. after heating to 50, and 300°C.

mer of ferrocene and α-naphthalene bromide (insoluble) whose electric conduction has changed by 5 orders. Evidently the degree of σ_{50} and E change is associated with peculiarities in the macromolecule structure of this polymer and with the surface structure.

Special attention ought to be paid to the $\sigma = \sigma(T)$ dependence of the polymer prepared by polycondensation of 1, 1′-diacetylferrocene with the $ZnCl_2$ catalyst (Fig. 5). As seen in this figure, the heating of this specimen under 1×10^{-4} mm. Hg up to 250°C. results in a sharp increase of its conduction (7 orders) and its activation energy ~1.5 e.v. (curve *1*, Fig. 5). Consequent heating and cooling of this specimen under 10^{-4} mm. Hg does not produce any noticeable change in its electric conduction (curve *2*). The activation energy during this treatment equals 0.05 e.v., which is already on the boundary of the measurement accuracy. If this specimen is placed in air, a gradual decrease of its electric conduction occurs. During the consequent heating under 10^{-4} mm. Hg (curve *3*) the electric conduction of this specimen again acquires its original value and curve *2* corresponds to the temperature characteristic of conduction.

The study of the curves in Figure 5 leads to the following conclusions. For polymer semiconductors in which the molecules are made up of a system of conjugated links it is necessary to differentiate the processes resulting from the motion of the current carriers within the macromolecule and their transition from one macromolecule to another. The influence of surface adsorption of the electron acceptor compounds (e.g., O_2) not only have an effect of the conduction value and on the value of the activation energy but it can change the sign of conduction, which from the electron conduction characteristic for the polymer semiconductors can become the hole conduction as has been shown[13,14] for pyrolyzed polyacrylonitrile. Therefore curve *1* in Figure 5 corresponds to the desorption which is under the exponential law; the activation energy (E = 1.5 e.v.), determined according to this curve is thus almost completely determined by the linkage of the adsorbate and the adsorbent and does not characterize the activation energy of the semiconductor. The true activation energy of the semiconductor is determined from curve *2* in the Figure 5 ($E \sim$ 0.05 e.v.); it characterizes the forbidden band in a molecule with a system of conjugated bonds as being very small.[14]

The comparatively high specific resistance of the prepared polymers is the result of potential barriers of transitions of the current carriers from one molecule to another.

As it is clear from curve *3* in Figure 5 the fact is that there is practically no temperature dependence. Therefore it is probable that the transition of current carriers from a macromolecule to another one occurs through tunneling, which is non-activation process.[14]

As seen from Table IV, heating under 1×10^{-4} mm. Hg at 200°C. does not result in complete desorption from the surface of the rest of the specimens. Evidently for these polymers a more severe pretreatment is necessary.

Conclusions

Fourteen new polymers based on ferrocene and its derivatives have been prepared by the reactions of polyrecombination and of polycondensation. Some of their chemical and electrophysical properties have been studied.

It is shown that the prepared polymers representing the polyconjugated systems have the properties of semiconductors. Their specific electric resistance is within the range of 1×10^{15}–1×10^{9}, and their activation energy is within the range of 0.3–1.74 e.v. (without desorption from the surface).

The role and influence of the surface adsorption on the semiconductive properties of the 1.1′-diacetylferrocene polymer have been elucidated.

The observed great energies of activation are to some extent the result of π-electron excitation from the valent region to the conduction region of macromolecules, but mainly the result of surface adsorption.

The sharp increase of conduction and the high melting point of all the studied polymers make it possible to use them for high temperature circuits in which it is necessary to have semiconductors with high resistance.

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Synopsis

A number of new polymers based on ferrocene were prepared and their electrophysical properties investigated. The polymers were obtained by different methods; from the

polyrecombination, i.e., by linkage (tailoring) of the primary monomers of ferrocene with a number of aromatic compounds (naphthalene bromide, *p*-dichlorobenzene, quinoline, benzonitrile, diphenyl, diphenylamine) in the presence of *tert*-butyl peroxide. The prepared polymers are black powders infusible up to 500°C. Approximately $^1/_3$–$^1/_4$ of a polymer is a soluble product and correspondingly $^2/_3$–$^3/_4$ are insoluble parts. Molecular weights of the soluble polymers are within the range of 2000–3000; elementary composition and Fe content are in good agreement with the given formulae. The polymers give a peak in the ESR spectrum. Polymers obtained from alkyl ferrocenes (from i-$C_4H_9C_5H_4FeC_5H_5$ $C_8H_{17}C_5H_4FeC_5H_5$), e.g. *tert*-butylferrocene, are soluble, and melt at 290–300°C. but these polymers do not give a peak in the ESR spectrum. Unlike benzene and its homologs, ferrocene forms high molecular compounds by polycondensation with acetone; these polymers have molecular weights of 3000–3200, melting points of 320–360°C., and give a peak in the ESR spectrum. Polycondensation of acetyl, alkyl acetyl, and diacetyl ferrocenes forms soluble and insoluble polymers giving a peak in the ESR spectrum. For a number of the prepared polymers electrophysical properties have been defined. Measurements of conductivity were made in vacuum (1×10^{-4} mm. Hg) by the compensation method within the temperature range of 20–200°C. All samples have a positive thermal coefficient of conductivity and in the investigated range of temperature are subjugated to the exponential dependency of conductivity on temperature $\sigma = \sigma_0 e^{-E/K \cdot T}$ which is characteristic of usual semiconductors. The value of specific electroconductivity at 50°C. is 1×10^{-15}–5×10^{-9} ohm^{-1} cm.$^{-1}$ and the activation energy is 1.74–0.30 e.v. The role and influence of the surface adsorption on the semiconductive properties of the polymers have been elucidated.

Résumé

Les auteurs de ce travail ont préparé un certain nombre de nouveaux polymères à base de ferrocène et ont étudié leurs propriétés électro-physiques. On a obtenu les polymères par différentes méthodes: par réaction de polycombinaison, par couplage des monomères primaires de ferrocène avec un certain nombre de composés aromatiques (bromure de naphtalène, *p*-dichlorobenzène, quinoléine, benzonitrile, diphényle, diphénylamine) à l'aide du peroxyde de *tertiaire*-butyle. Les polymères préparés sont des poudres noires, infusibles jusqu'à 500°. Environ $^1/_3$–$^1/_4$ d'un polymère est un produit soluble et les autres $^2/_3$–$^3/_4$ sont des parties insolubles. Les poids moléculaires des polymères solubles se situent entre 2000–3000, la composition élémentaire et la teneur en fer correspondent bien avec la formule donnée. Les polymères fournissent un maximum dans le spectre ESR. La recombinaison d'alcoyles ferrocènes (depuis i-$C_4H_9C_5H_4FeC_5H_5$ jusquà $C_8H_{17}C_5H_4FeC_5H_5$) p.e., du *tertiaire* butyle ferrocène donnent des polymères solubles, qui fondent à 290–300°, mais ces polymères ne donnent pas un maximum dans le spectra ESR. Contrairement au benzène et à ses homologues le ferrocène forme des produits de haut poids moléculaire par polycondensation avec l'acétone. Qui ont un poids moléculaire de 3000–3200, un point de fusion de 320–360° et qui ont un maximum dans le spectre ESR. La polycondensation des acétyle, alcoyle acétoyle et diacétoyle ferrocènes forment des polymères solubles et insolubles. Qui donnent un maximum dans le spectre ESR. On a défini pour un certain nombre de polymères préparés les propriétés électrophysiques. Des mesures de conductivité ont été faites sous un vide de 1×10^{-4} mm de mercure par la méthode de compensation dans un intervalle de 20–200°C. Tous les échantillons ont un coefficient thermique positif de conductivité et dans le domaine de température étudié sont soumis à la dépendance exponentielle de la conductivité vis-à-vis de la température $\sigma = \sigma_0 e^{-E/KT}$, ce qui est caractéristique pour les semiconducteurs ordinaires. La valeur de la conductivité électrique spécifique à 50° est de 1×10^{-15} à 5×10^{-9} ohm^{-1} cm.$^{-1}$ et l'énergie d'activation est de 1.74 à 0.30 e.v. On a étudié le role et l'influence de l'adsorption de surface sur les propriétés semi-conductrices des polymères.

Zusammenfassung

Die Autoren der vorliegenden Arbeit stellten eine Anzahl neuer Polymerer auf Ferrocenbasis her und untersuchten ihre elektrophysikalischen Eigenschaften. Die Polymeren wurden nach verschiedenen Methoden dargestellt, von denen zunächst die Polyrekombination, d.h. die Verknüpfung des primären Ferrocen-Monomeren mit einer Anzahl aromatischer Verbindungen (Naphthylbromid, *p*-Dichlorobenzol, Chinolin, Benzonitril, Diphenyl, Diphenylamin) mittels *tert.*-Butylperoxyd, beschrieben wird. Die so hergestellten Polymeren sind bis hinauf zu 500° unschmelzbare schwarze Pulver. Etwa $^1/_3$–$^1/_4$ des Polymeren ist löslich, die restlichen $^2/_3$–$^3/_4$ unlöslich. Das Molekulargewicht des löslichen Polymeren liegt zwischen 2000 und 3000 und die Elementarzusammensetzung und der Eisengehalt stimmen mit der angegebenen Formel gut überein. Die Polymeren zeigen im ESR-Spektrum ein Maximum. Die bei der Polyrekombination von Alkylferrocenen (von *i*-$C_4H_9C_5H_4FeC_5H_5$ bis $C_8H_{17}C_5H_4FeC_5H_5$), z.B. von *tert.*-Butylferrocen entstehenden Polymeren sind löslich, schmelzen bei 290–300°, geben jedoch im ESR-Spektrum kein Maximum. Im Gegensatz zu Benzol und seinen Homologen bildet Ferrocen durch Polykondensation mit Aceton hochmolekulare Verbindungen mit einem Molekulargewicht von 3000–3200, die bei 320–360° schmelzen und im ESR-Spektrum ein Maximum zeigen. Die bei der Polykondensation von Acetyl-, Alkylacetyl- und Diacetylferrocenen entstehenden löslichen und unlöslichen Polymeren geben im ESR-Spektrum ein Maximum. Es wurden die elektrophysikalischen Eigenschaften einer Anzahl der hergestellten Polymeren bestimmt. Die Leitfähigkeitsmessungen wurden im Vakuum (1.10^{-4} mm Quecksilbersäule) nach der Kompensationsmethode im t°-Bereich 20–200°C durchgeführt. Alle Proben haben einen positiven Temperaturkoeffizienten der Leitfähigkeit und folgen im untersuchten Temperaturbereich der für die üblichen Halbleiter charakteristischen exponentiellen Temperaturabhängigkeit der Leitfähigkeit $\sigma = \sigma_0 e^{-E/KT}$. Die spezifische elektrische Leitfähigkeit bei t° = 50° leigt zwischen 1.10^{-15} und 5.10^{-8} Ohm^{-1} cm^{-1} und die Aktivierungsenergie zwischen 1.74 und 0.47 e.V. Die Rolle und der Einfluss der Oberflächenadsorption auf die Halbleitereigenschaften der Polymeren wurden aufgeklärt.